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VOLUME 22, NUMBER 5

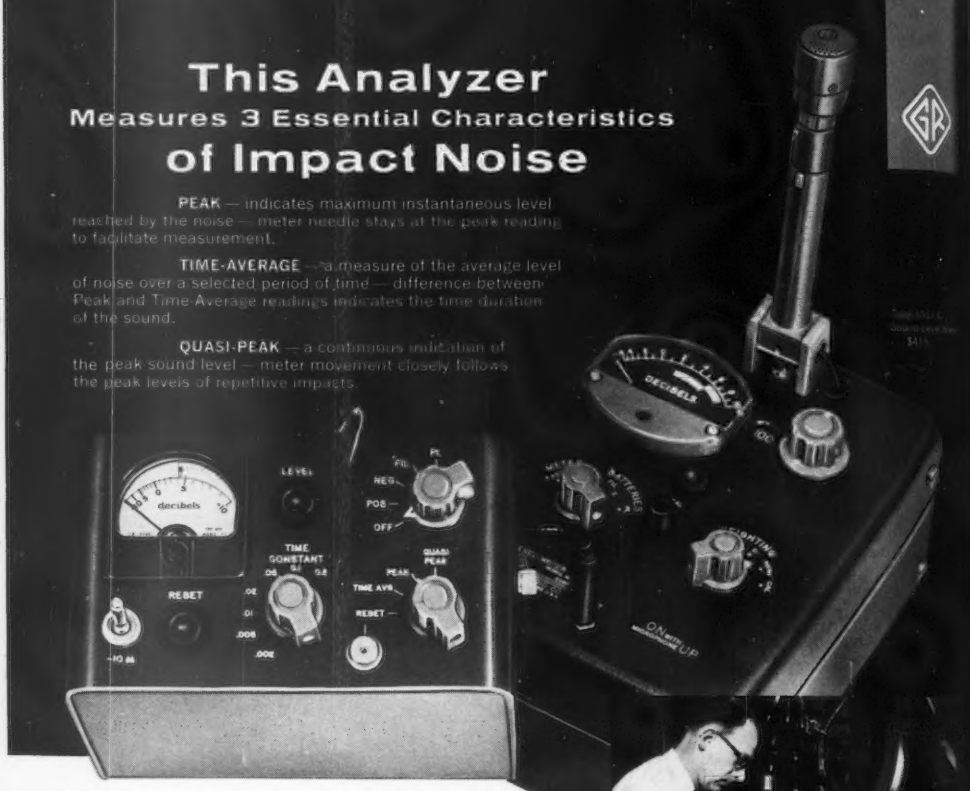
October 1961

This Analyzer
Measures 3 Essential Characteristics
of Impact Noise

PEAK — indicates maximum instantaneous level reached by the noise — meter needle stays at the peak reading to facilitate measurement.

TIME-AVERAGE — a measure of the average level of noise over a selected period of time — difference between Peak and Time-Average readings indicates the time duration of the sound.

QUASI-PEAK — a continuous indication of the peak sound level — meter movement closely follows the peak levels of repetitive impacts.



An electrical storage system retains the "Peak" and "Time Average" readings, regardless of the function setting of the instrument, so that these impact characteristics can be read at the operator's convenience. The convenient push-button reset switch, which erases the stored level, facilitates repetitive measurements.

Type 1556-B IMPACT-NOISE ANALYZER .... $220.

The Impact-Noise Analyzer is designed specifically for the measurement of impact noises such as the disconcerting and sometimes harmful sounds produced by punch presses, drop hammers, metal shears, firearms, office machines, and other noisemakers. Sound and vibration measuring equipment designed for steady-state analysis is inadequate for measuring the short-duration transients characteristic of impact noise. Complicated and bulky arrays employing oscilloscopes are impractical for in-the-field measurements. The battery-operated Impact-Noise Analyzer, attached to the end plate of the G-R Type 1551-C Sound-Level Meter, forms a compact package weighing less than 13 pounds.

Used in conjunction with the Sound-Level Meter, w serves as a preamplifier, the Impact-Noise Analyzer m ures the noise of this punch press. The instrument also be used with spectrum analyzers (such as G-R's 1550-A, Octave-Band Noise Analyzer) for frequency yses of impact sounds.

Write for the Sound Measuring Equipment Bulletin

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A Wind Tunnel for Providing Known Air Movement

RICHARD S. BRIEF and FRANKLIN W. CHURCH

Medical Research Division, Esso Research & Engineering Company, Linden, New Jersey

Unique features have been incorporated into a subsonic wind tunnel to simplify calibration of a wide variety of air flow instruments used in industrial hygiene, ventilation, and air pollution activities.

IN THE past, sub-sonic wind tunnels have been troubled by poor velocity contours, were unable to give a flat velocity contour even with air straighteners, and demonstrated varying fan performance with changes in the volume of air handled. More recent data, however, have made it possible to overcome these difficulties to the end that excellent performance can now be expected from a well-designed unit.

The wind tunnel described in the following paragraphs was designed to operate at sub-sonic velocities and incorporates a number of unique features. The tunnel provides velocities ranging from about 20 to 5000 fpm and flat velocity profiles in three different locations. Air flow instruments used in industrial hygiene, ventilation, and air pollution activities have been calibrated in this tunnel by comparing true flow versus scale readings at several points within the specific instrument's range. The wind tunnel can also be used to evaluate the performance of special hood shapes.

Design and Operation Features

The wind tunnel was designed to provide two different cross-sectional calibration areas on the inlet side so as to simultaneously give two different velocities at each volume setting. An additional calibration area is provided on the outlet or exhaust side to provide a convenient means of checking supply opening jets and of calibrating large-sized velocity-sensitive probes under high

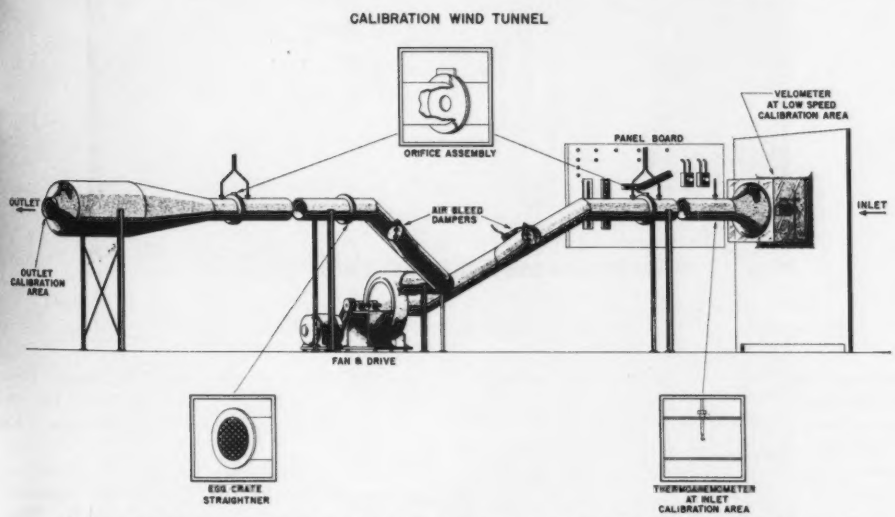

FIGURE 1. A descriptive sketch of the wind tunnel apparatus for providing known air movement in the sub-sonic range.

FIGURE 2. A type 3930 Velometer probe being calibrated at the low-speed calibration area. The panel board can be seen through the lucite test section.

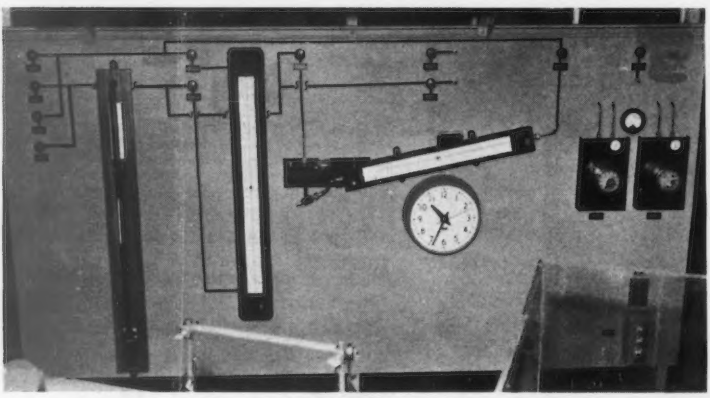

FIGURE 2A. The panel board used with the wind tunnel. A barometer, vertical and inclined manometers, and the valves for the pneumatic controllers can be seen from left to right.

velocity conditions. The complete unit is shown schematically in Figure 1. Figures 2, 2A, 2B, 2C show the various sections in detail.

The three calibration areas provided are: (1) a "low-speed" section on the inlet side of the fan, (2) an inlet "high-speed" section at the throat of a properly shaped nozzle, and (3) a similar "high-speed" section on the outlet side of the fan at the throat of another properly shaped nozzle. The nozzles are untrimmed sousaphone bells which have excellent aerodynamic properties. These stock item sousaphone bells accounted for considerable savings in the construction costs of the wind tunnel.

One metering orifice assembly is located on either side of the fan. Two ASME-specified[1] orifices are provided for each assembly. These orifices were sized to meter the full range of flows that would be encountered.[2]

An air bleed line with a pneumatically-con-

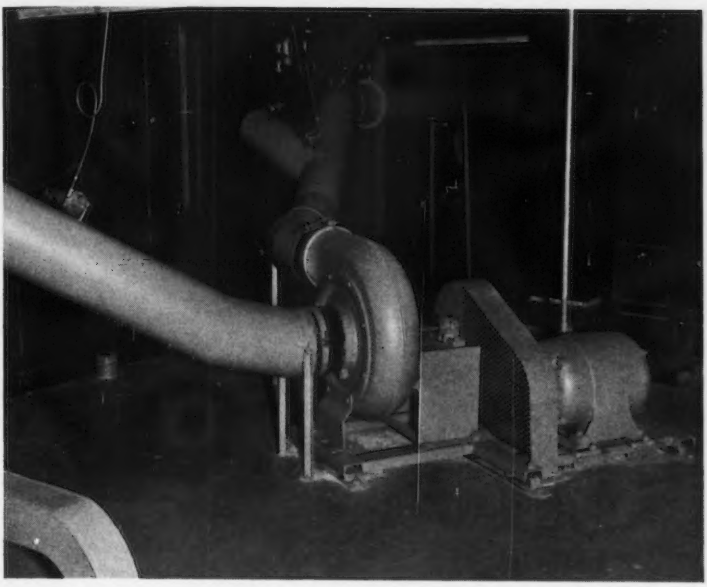

FIGURE 2B. A view of the motor-fan area. The pneumatic controllers for the air-bleed dampers can be seen on top of the ductwork.

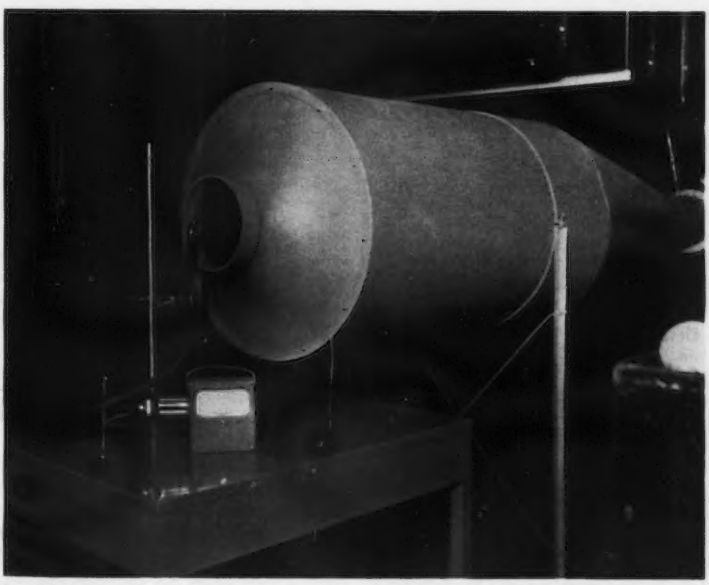

FIGURE 2C. The outlet calibration area is shown being used to calibrate a 3920 supply opening probe for a Velometer.

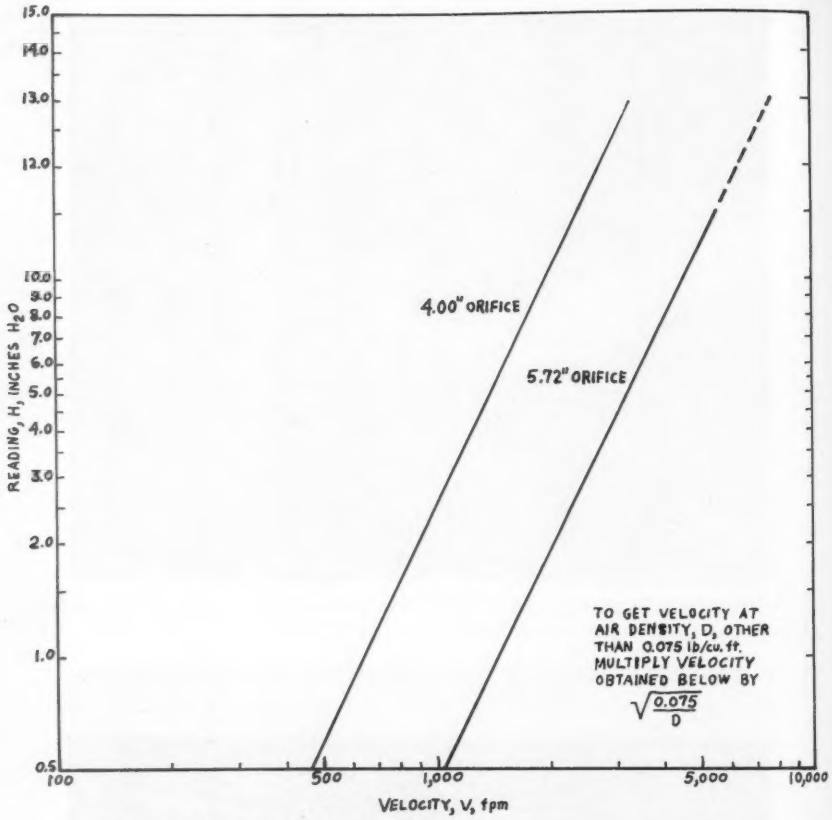

FIGURE 3. Velocity at 8" diameter inlet calibration area vs orifice reading.

trolled damper is positioned on either side of the fan to help vary the air flow through the calibration areas and to allow operation within the most stable region of the fan's curve. The fan is belt-driven by a two-speed five-horsepower motor to provide additional flexibility in operation.

Construction Details

The inlet air is drawn into a 2½ ft square x 2 ft deep lucite test section, with a 7½ ft square steel intake flange. A smooth entrance shape is provided to reduce turbulence in the low-speed calibration area. The air in the lucite box is then accelerated through a bell-mouth into a carefully honed 8 in. inside diameter brass pipe. The throat of the bell mouth serves as the second test zone or inlet calibration area.

The air then moves through the 8 in. ductwork, past an orifice assembly where it is metered, and on to the intake side of the fan. Additional air can enter at the intake side of the fan through an air bleed line with a pneumatically-controlled damper. The air continues through the fan and can either be exhausted through another air bleed, again with a pneumatically-controlled damper, or pass through an egg-crate straightener and on past the second orifice assembly. In the latter case, the flow then continues to an expanded section and is accelerated through another bell-mouth shape, discharging through an outlet of 8¼ in. inside diameter. This discharge zone is the outlet calibration area.

Initially the orifice plates, which are equipped with 1-D and ½-D pressure taps, were calibrated with an NPL standard round-nosed pitot-static tube traversing the throats of the bell-mouth shapes in the wind tunnel. A Hook gauge was used to measure the velocity pressure from the pitot-static tube to 0.001 in.

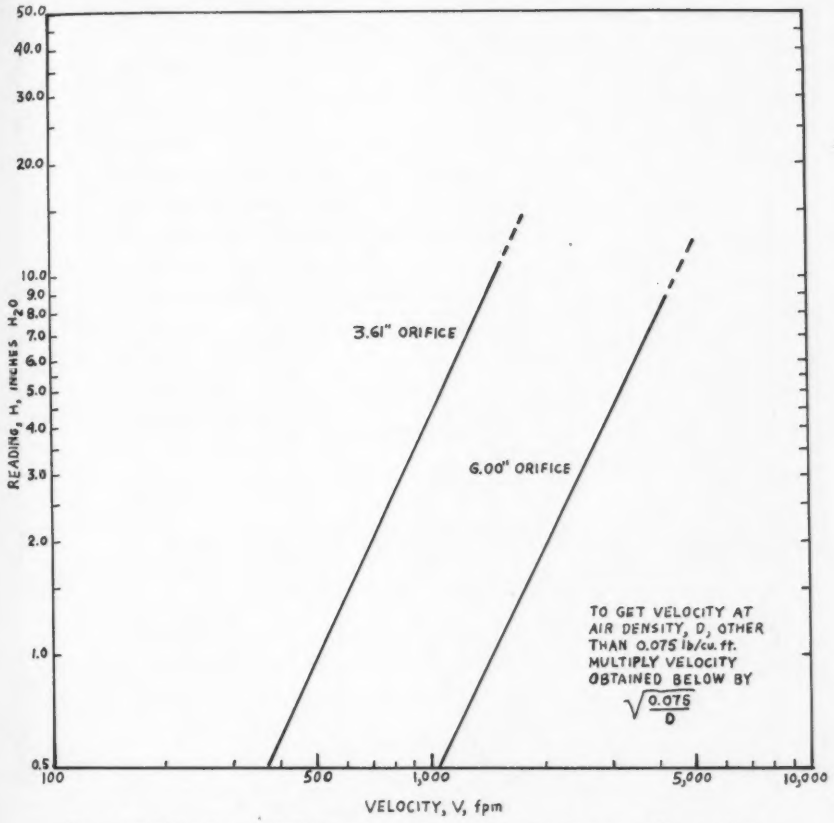

FIGURE 4. Velocity at 8.25" diameter outlet calibration area vs orifice reading.

H_2O. The flow through these bell-mouth shapes or nozzles was constant across the full cross-sectional area, as predicted by theory.[3] This uniform profile simplified the traverse procedure and assured the accuracy of the orifice calibrations. The orifice calibration curves are shown in Figures 3, 4, and 5. Figure 6 shows the worksheet used in routine testing of air-sensitive probes.

Instruments successfully calibrated to date are listed in Table I. Deviations as great as 50% from the expected reading were noted in some of the air-sensitive probes tested.

Volumes up to about 1700 cfm free delivery can be checked with this device. The technique requires fabricating a baffle to fit the wind tunnel to insure that all the air being metered by an orifice is actually passing through the unit being evaluated. Such units can be instruments, like high-volume samplers, hood shapes, metering assemblies, and the like. Three projects utilizing this approach have been completed.

Accuracy

Total volume delivered or metered by various instruments can be checked with the wind tunnel in the range 200–1700 cfm, or from about 20–5000 fpm. Lower volumes can be checked, but at decreasing accuracy. In the operating range of velocities used, the 95% confidence internal is nominally ± 2% of the velocity determined from the calibration charts. (See Figures 3, 4, and 5.) In order to gain greater accuracy, if it is desired, the calibration runs are arranged so that the orifice reading used is actually the mean of five individual determinations at the same air flow setting. By this technique, the 95% confidence interval is reduced to about ± 1% of the velocity. The statistical development used has been described by Davies.[4]

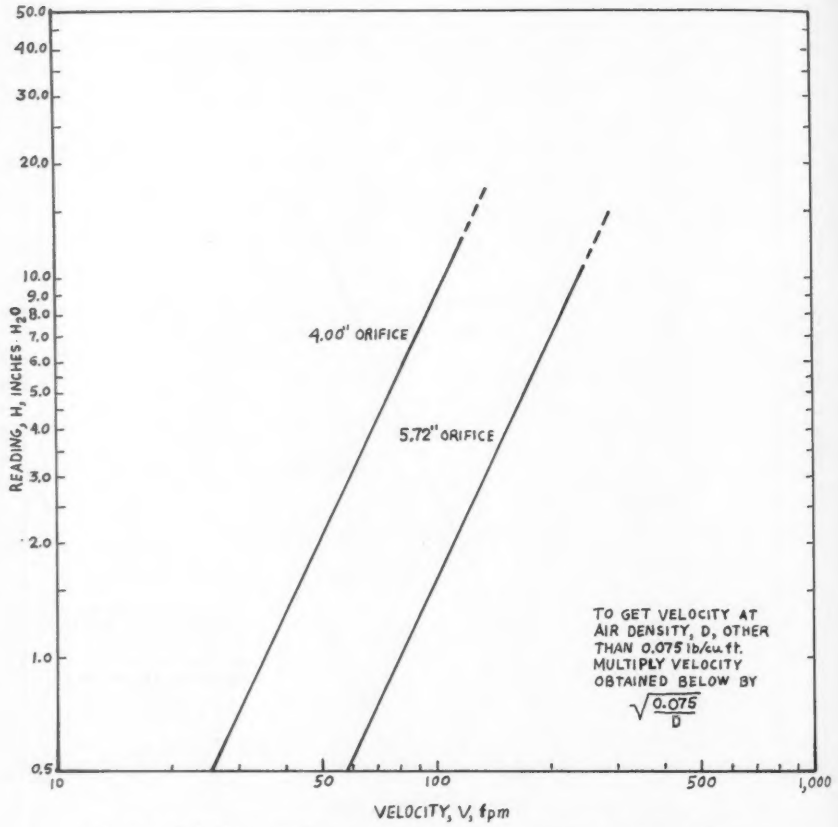

FIGURE 5. Velocity at low speed inlet calibration area vs orifice reading.

Other Calibration Methods

In addition to the wind tunnel, there are two other accepted types of air flow calibration devices: the whirling arm and the linear track.[5] Some of the inherent disadvantages of these two methods are described below.

Centrifugal Effects

At greater than 300 fpm peripheral velocity, centrifugal effects would be noticeable in the whirling arm. If the speed is further increased, the radius of the whirling arm should likewise be increased to avoid these forces as much as possible.

Induced Flow or Swirl

Induced flow is also significant in a whirling arm apparatus. The magnitude of the swirl was found to be up to 16% of the velocity in an enclosed whirling arm device and about 6% of velosity in an open whirling arm device.[6, 7, 8, 9] In both enclosed and open linear tracks, there is some induced flow. The distinction between "open" and "enclosed" refers specifically to a housing placed around the device to cut down on the induced flow and natural effects.

Vertical Motion and Natural Air Currents

There is some additional motion in the vertical direction in both the open whirling arm and open linear track methods. Enclosing these devices tends to reduce or eliminate these effects.

Electrical Response Instruments

Calibration on the whirling arm and linear track of instruments that depend upon small changes in electrical values is difficult because of necessarily long transmission lines, commutators,

WIND TUNNEL WORK SHEET

Instrument:

Probe:

Fan Speed:

Orifice Size: 4.00", 5.72", 3.61" 6.00"

Operating Side: Inlet, Outlet

Calibration Area: 8" Diam., Lucite, 8 1/4" Diam.

T: Dry Bulb Temp. _____°F

Wet Bulb Temp. _____°F

Humidity: _____ gr. H_2O/lb. dry air

G: Specific Gravity:

P: Barometer: _____" Hg.

D: Density = $1.325 \frac{PG}{T}$ = _____ lb./cu. ft.

$\frac{.075}{D}$ = $\sqrt{\frac{.075}{D}}$ =

Average Orifice Reading, H.	No. of Detns. Used in Avg. H.	From Chart, Velocity at D = .075	True Velocity, fpm $V = V_{.075} \times \sqrt{\frac{.075}{D}}$	Instrument Indication, fpm

FIGURE 6. Worksheet used in calibration of velocity-sensitive probes.

TABLE I

Instruments Calibrated

Instrument	Manufacturer	Total No. of Probes Tested	Indicated Velocity Range, fpm
Alnor Velometer, Type 3002	Illinois Testing Laboratories, Inc.	22	20–300 100–1000 500–6000
Precision Air Meter, Model B-15	Hastings-Raydist, Inc.	2	0–500 500–20,000
Thermo-anemometer, Type 8500	Illinois Testing Laboratories, Inc.	2	10–300 100–2000
Thermo-anemometer, Model GGA2C	Gelman Instruments Company	1	6–1800
Heated Thermometer-Anemometer	Willson Products, Inc.	6	10–6000

and amplifying equipment. The wind tunnel has no such drawback.

Length

The linear track must be made very long to measure high velocities; thus its use is practically limited to low velocity calibration. Assuming about three seconds for steady state, 300 ft of accurately aligned track would be necessary to measure a velocity of 6000 fpm. Also, extra length would have to be provided for acceleration and deceleration.

The wind tunnel has none of the above disadvantages. It is finding increased acceptance as the basic calibration standard for air flow calibration, replacing the other two devices noted.

References

1. American Society of Mechanical Engineers: *Flow Measurement*. Report PTC 19.5:4, ASME, New York (1959).
2. BRIEF, R. S.: Chart Speeds Orifice Selection. *Air Cond., Heat. and Vent. 57*(8): 57–60 (August, 1960).
3. OWER, E.: *The Measurement of Air Flow, 3rd Edition, Revised*. Chapman and Hall, Ltd., London (1949).
4. DAVIES, O. L.: *Statistical Methods in Research and Production, 3rd Edition*. pp. 169, 170. Hafner Publishing Company, New York (1958).

5. Hill, W. W.: *Study of Calibration Devices for Wind-Measuring Equipment. Project Report No. 2, Analysis of Methods of Calibration.* Purdue University School of Aeronautical Engineering. Report No. A-57-11 (Dec. 1957).
6. Ferguson, S. P.: *Experimental Studies of Anemometers.* Harvard Meteorological Studies, No. 4 (1939).
7. Cowdrey, C. F.: A Note on the Calibration and Use of a Shielded Hot-Wire Anemometer for Very Low Speeds. *J. Scient. Instr. 27:* 327 (Dec. 1950).
8. Hromas, L. A., and C. P. Kentzer: *Calibration on a Hot-Wire Anemometer for Low Velocities in Steady Flow with Temperature Gradients.* Purdue University School of Aeronautical Engineering. Report No. A-55-1 (1955).
9. Simmons, L. F. G.: A Shielded Hot-Wire Anemometer for Low Speeds. *J. Scient. Instr. 26:* 407 (Dec. 1949).

Program Planning

THE PROGRAM PLANNERS for the Twenty-third Annual Meeting of the American Industrial Hygiene Association to be held at the Park-Sheraton Hotel, Washington, D.C., May 13–17, 1962, have been hard at work preparing an interesting and informative program from the papers offered for presentation. While many of the selections have already been made firm, there is yet time to receive and consider additional papers for this meeting. Inasmuch as the program must be well-shaped before December, persons desiring to make a last minute submittal of a paper should act immediately to send their subject and something concerning the paper to the appropriate Session Arranger or the Chairman. Abstracts of all papers are desired by January 1 and will be required by February 1, 1962. All papers presented at the annual meetings of the American Industrial Hygiene Association are considered for publication in the AIHA Journal.

Following are the names and addresses of the Program Chairman and the Session Arrangers:

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525 William Penn Place
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Engineering
Isaac Matelsky
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Radiation
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Removal of Solid Particles from a Solid Surface by a Turbulent Air Stream

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Ground silica dust ($Mg = 1.3\ \mu$, $\Sigma g = 1.7$) was deposited on Tyler 100 mesh screen at velocities from 3.8 to 27 fps. Particles adhering to the screen were then blown off by filtered air at velocities greater than deposition. Air drag on particles submerged in the laminar boundary layer was calculated from a simple irrotational fluid flow model and compared to particle adhesion force determined in a companion study. Air drag calculated in this manner failed to account for observed particle re-entrainment. Particle re-entrainment, defined in terms of screen pressure loss, was more difficult to achieve as deposition velocity increased. A blowoff velocity of 132 fps, based on screen free cell area, removed essentially all adhering dust from a single screen. During both deposition and dust blowoff procedures, the collector acted as a particle agglomerator and increased particle size by a factor of approximately 2×.

Introduction

UNTIL recently all theoretical approaches to filtration mechanism in air were based on adhesion of particle to fiber after occurrence of initial contact.[1-7] Unusual results by Ramskill and Anderson[8] during filtration experiments suggested non-adherence of impinging particles to Gillespie and Rideal.[9, 10] A subsequent investigation by Gallily and La Mer[11] confirmed that non-adherence of liquid droplets was velocity dependent. The behavior of solid particles on impact at solid surfaces is less clearly defined than for liquid droplets.

Cloth or fabric filters operated at air velocities above 50 fpm or above approximately 200 fpm for air conditioning or roughing filters such as the coarse glass fiber type, are considered high velocity filters. Lapple *et al.*[12] observed particle blowoff from such filters operating at air velocities from 3 to 10 fps.

In contrast to particle non-adherence during filtration, particle re-entrainment during filter cleaning operations is desirable. Fabric filters are usually rapped, shaken, or cleaned by reverse air or air jets. Recent investigations suggest the utilization of shock waves for such cleaning.[13]

Particle re-entrainment during filtration and filter cleaning cycles are phenomena intimately associated with the forces of adhesion holding particles to surfaces and to each other. Early investigations of Bagnold[14] dealt with wind re-entrainment of sand grains larger than 80 microns. Gutterman and Ranz[15] treated the case of dust re-entrainment in ducts but found it necessary to characterize shear properties of individual dust layers in order to approximate re-entrainment velocities. Rumpf[16] related particle adhesion to fluid drag, as contrasted to some special function of particle or bed weight. However, he lamented the lack of adhesion data to complete the analysis. Recently, Kordecki and Orr[17] theoretically related air drag to particle adhesion forces actually determined by a centrifuge technique. They concluded that natural forces other than rain were not sufficiently strong to dislodge solid particles adhering to solid surfaces in air.

In a companion study which preceded this experiment, forces of adhesion of micron size particles to solid surfaces in air were measured by a micromanipulative technique employing a microbalance.[18] It was of great practical importance to know if basic particle adhesion data could be extrapolated, even approximately, to predict re-entrainment from a solid surface transverse to an air stream. Therefore, this experiment was undertaken. While pursuing this objective, interesting results were obtained relative to dust re-entrainment during deposition and after deposition when clean air was applied to remove particles adhering to the collector surface. In this paper, the theoretical model used to predict re-entrainment will be described first. This will be followed by a description of the experiment. It should be noted that relatively large scale equipment was specifically selected to

see if re-entrainment predictions could bridge the gap from individual laboratory adhesion measurements to a pilot scale system.

Theory

In this study comparison was made between particle adhesion forces and air velocities which re-entrained particles residing on cylindrical test surface fibers. To do this, air drag acting on particles submerged in the laminar boundary layer of a cylinder was calculated by means of a simple model. The procedures and assumptions involved in these calculations are outlined below.

The simplified two-dimensional equation of motion in the boundary layer for incompressible fluid flow past a curved surface is:[19]

$$u\frac{\partial u}{\partial x}+\nu\frac{\partial u}{\partial y}=-\frac{1}{\rho}\frac{\partial P}{\partial x}+\frac{\mu}{\rho}\frac{\partial^2 u}{\partial y^2} \qquad (1)$$

In addition, the two dimensional continuity equation for the boundary layer is given by Eq. (2).

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0 \qquad (2)$$

Since u is the velocity in the x direction only and does not vary in the y direction, Bernoullis' equation holds for the boundary layer.

$$\frac{P}{\rho}+\frac{u^2}{2}=\text{constant} \qquad (3)$$

and

$$-\frac{1}{\rho}\frac{\partial P}{\partial x}=u\frac{\partial u}{\partial x} \qquad (4)$$

Substituting Eq. (4) in Eq. (1) yields:

$$u\frac{\partial u}{\partial x}+\nu\frac{\partial u}{\partial y}=u\frac{\partial u}{\partial x}+\frac{\mu}{\rho}\frac{\partial^2 u}{\partial y^2} \qquad (5)$$

Meksyn[20] solved equations (2) and (5) for the case of a circular cylinder by assuming that velocity at the edge of the boundary layer varies the same as if the flow were not rotational. Thus, if u^* is the velocity at the edge of the boundary layer, Meksyn assumed

$$u^*=2U\ \text{Sin}\ \theta \qquad (6)$$

and Eq. (5) can be rewritten as

$$u\frac{\partial u}{\partial x}+\nu\frac{\partial u}{\partial y}=u^*\frac{\partial u^*}{\partial x}+\frac{\mu}{\rho}\frac{\partial^2 u}{\partial y^2} \qquad (7)$$

Meksyn showed that his solution to the boundary layer equations (2) and (7) compared favorably with wind tunnel measurements of boundary layers on circular cylinders. In this study, his solution has been used to calculate velocities at the edge of the boundary layer on circular fibers exposed to a main stream air velocity U. Computational tables given by Knudsen and Katz[21] were used.

In the laminar boundary layer, velocity is proportional to the normal distance from the surface up to the edge of the layer where $u = u^*$. Therefore, u at any point in the boundary layer can be found after u^* is known.

The drag force on a particle on a cylindrical fiber at any angle θ from the forward stagnation point was assumed to act at normal distance $\frac{1}{2}D_P$ from the cylinder surface and to be due to the boundary layer velocity at $\frac{1}{2}D_P$ (Eq. 8). Particle Reynolds number was calculated from Eq. 9 and C_D was obtained from appropriate curves of Re vs. C_D.

$$F_D=\frac{C_D\rho u^2 A\rho}{2} \qquad (8)$$

$$\text{R}_e=\frac{D_p\rho u}{\mu} \qquad (9)$$

Drag was calculated for a sphere completely immersed in an air stream, *i.e.* fluid disturbance due to the fiber was ignored.

In summary, steps involved in calculation of drag on individual particles residing on test surface fibers were:

1. Calculate u^* at point θ from stagnation point.
2. Calculate u at $\frac{1}{2}D_P$ in boundary layer.
3. Calculate R_e at $\frac{1}{2}D_P$.
4. Calculate F_D.

Inherent in these calculations are the following assumptions: (1) non-disturbance of the boundary layer due to particle and adjoining fibers, (2) spherical particles, (3) negligible air lift on the particle, (4) air drag on the particle is the only removal force.

Equipment and Procedures

Test System

Figure 1 is a schematic drawing of the test system which provided filtered room air at deposition surface approach velocities to 3050 cm/sec (100 fps). All straight runs were 2½" nominal size seamless Type K copper tubing (6.15 cm i.d.). At the lowest dust deposition velocity employed, *i.e.* 116 cm./sec (3.8 fps), Reynolds number in the test duct was 3,650. Therefore, during all tests, the air stream used to deposit and re-entrain dust was in turbulent motion as

it approached the dust collecting surface. Transition sections and Venturi meter were fabricated from No. 24 galvanized sheet metal and adjoining duct pieces were joined by flanges with Neoprene rubber gaskets. Pressure taps, sampling tubes and dust feed tube were copper tubing (¼"). All air entering the test duct passed through a plenum chamber and MSA Ultra-aire filter rated at 99.99% efficiency for 0.3 micron dust (DOP).

The primary air mover was a Spencer turbocompressor (Spencer Turbine Co., Hartford, Conn.) rated at 240 cfm against 8 oz. head. Air velocity in the duct was controlled by a butterfly valve in the blower exhaust duct and was monitored by a Venturi meter calibrated against an impact velocity micropitot tube with static pressure wall tap. Pitot tube coefficient was assumed to be 1.0 and twelve-point duct traverses were made. Maximum metering error occurred at low air flows and is estimated as not exceeding ±5%. There was sufficient straight run before the deposition surface as evidenced by symmetrical duct velocity distributions.

Test Dust

The test dust was ground silica (99.9% SiO_2) ($Mg = 1.10\ \mu$, $\Sigma g = 1.7$). It was sampled isokinetically in the test duct with a probe incorporating a settling chamber with glass microscope slide at the base. Settled dust was sized under high, dry magnification (900×) by an optical microscope calibrated with a Porton graticule.

Dust entered the test duct from either a Harvard Turntable Feeder[22] or a Wright Dust Feed.[23] The latter device delivered dust at loadings less than approximately 250 mg/m³, while the former was satisfactory at higher loading. Clogging of the outlet tube at high dust loadings prevented use of the Wright Dust Feed in all runs.

Compressed air required to operate the Wright Dust Feed was dried ($CaCl_2$), filtered (1106B Glass Web paper), regulated and metered by calibrated rotameter. In all tests this stream of air represented a small fraction of total air in the test duct. At the lowest deposition velocity of approximately 91 cm/sec (3 fps) it contributed 5% of total duct air.

Aerosol Sampling Procedures

Air-borne dust particle size determination is described above. Dust loading upstream and downstream of the test surface was determined with isokinetic sampling probes described by Anderson.[24] The probes contained 22 mm circles of 1106B glass web filter paper which were weighed before and after sampling on a semi-micro analytical balance (±0.0001 g). Average

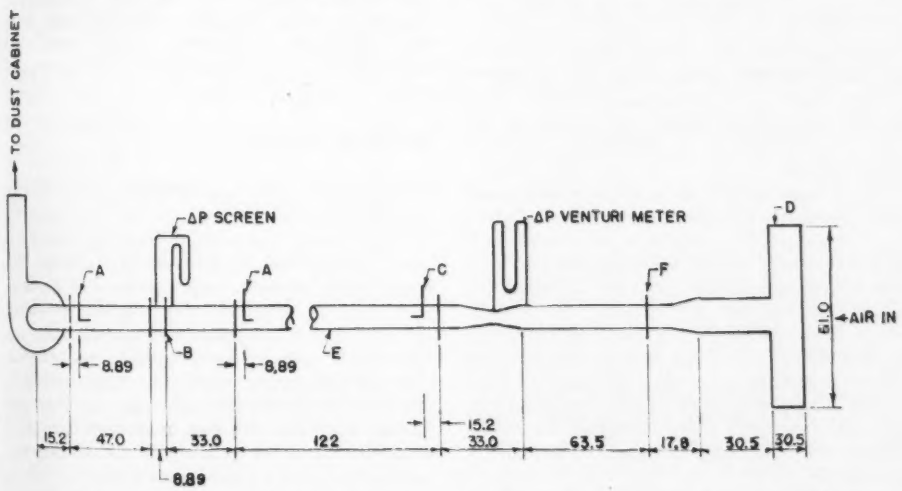

FIGURE 1. Schematic of dust re-entrainment test system. (Note: All dimensions are in centimeters.)

A—Sampling Probe
B—Test Screen
C—Dust Feed
D—MSA Ultra-aire Filter
E—2½" Copper Tubing
F—Flange

sample weights of two to four milligrams indicate a possible weighing error of 5.0 to 2.5%. All dust sampling trains utilized spirometer calibrated orifices (±2%) to meter air flow.

Dust Deposition Surface

The ideal test surface, one which could be used to accurately evaluate aerosol removal mechanisms, is a series of parallel, uniform fibers of known diameter and spacing. Difficulties encountered in fabrication of an "ideal" surface led to adoption of Tyler 100 mesh woven metal screens for these studies. Disadvantages associated with crossing of warp and woof in this material are offset by uniformity of fibers and spacings, availability, and ease of static change removal by simple grounding.

Tyler 100 mesh screen is composed of fibers with 120 micron diameters and spacings between fibers of 147 microns. Screen free cell area is 30.4%. Therefore, all duct air velocities must be multiplied by a factor of 3.3 to obtain mean air velocity through the clean screen void area. Dust trapped in test screen pores serve to increase this factor.

At the lowest flow condition of 116 cm/sec (3.8 fps) air approach velocity, Reynolds number based on screen fiber size was approximately 32, indicating that fluid motion past the cylindrical fibers composing the screen was not streamline.

Test Procedures

Assessment of dust re-entrainment after collection by test screens was of primary interest in this experiment. Dust collection efficiencies of the screens were not determined, but were below the detection limit of aerosol samples, *i.e.* less than 5% by weight.

Oil or water manometers (1:10 incline) were used to measure pressure loss through the screen as a function of time for each test condition of duct air velocity and dust loading. Aerosol samples were obtained simultaneously upstream and downstream of the test surface. Eventually, pressure loss through the dust laden screen reached equilibrium. Dust feed, aerosol sampling and main air flow were then terminated. Aerosol sampling probes were removed from the system and new probes were inserted to obtain downstream dust samples during re-entrainment procedures.

Re-entrainment of dust residing on the Tyler screen was accomplished by adhering to the following sequence of operations:

1. Adjust duct air flow for deposition velocity and confirm equilibrium pressure loss. Check pressure loss at lower velocities.
2. Increase dust air velocity to predetermined level above that of deposition and hold for one minute.
3. Lower duct air velocity to deposition velocity and record new pressure loss.
4. Repeat steps 2 and 3 with progressively higher air velocities until pressure loss through the test screen is equal to that of the clean screen, or until blower capacity is reached.

One minute was chosen for dust laden screen exposure time on the basis of dust removal achieved with filters exposed to blast waves which act for fractions of a second.[25] Observations during these tests indicate that if the dust comes off the test surface, it does so almost immediately after exposure to the high velocity air stream. Dust laden screen pressure loss did not fall during the entire minute of exposure; it fell immediately after exposure. A one minute exposure permitted all downstream aerosol sampling adjustments, pressure readings, etc. to be conveniently made.

Measurement of Dust Captured by Screen

It would have been desirable to remove the test screen from the duct and weigh the dust remaining on the screen after each successive treatment with high velocity air. However, this procedure would have disturbed the deposit. Therefore, dust deposited on the screen was indirectly monitored by pressure loss through the dust laden screen. The differences between dust laden and clean screen pressure losses were used to define effectiveness of dust removal from the screen by high velocity air.

Results and Discussion

Characteristic Dust Deposition and Re-entrainment Pattern

Regardless of dust loading or deposition velocity of the air stream, pressure loss through the single Tyler 100 mesh screen eventually reached a limiting, equilibrium value. Typical pressure loss-time curves are shown in Figure 2. Also indicated are pressure losses through the surface following application of specified clean air velocities for one minute intervals. All velocities are average approach velocities in the test duct, and should be multiplied by 3.3 to obtain average velocities through the clean screen voids.

Several conclusions can be drawn from Figure 2 and other similar data:

1. At each deposition velocity, regardless of stream loading, pressure loss through the test screen reached a reproducible equilibrium value. At any deposition velocity dust loading

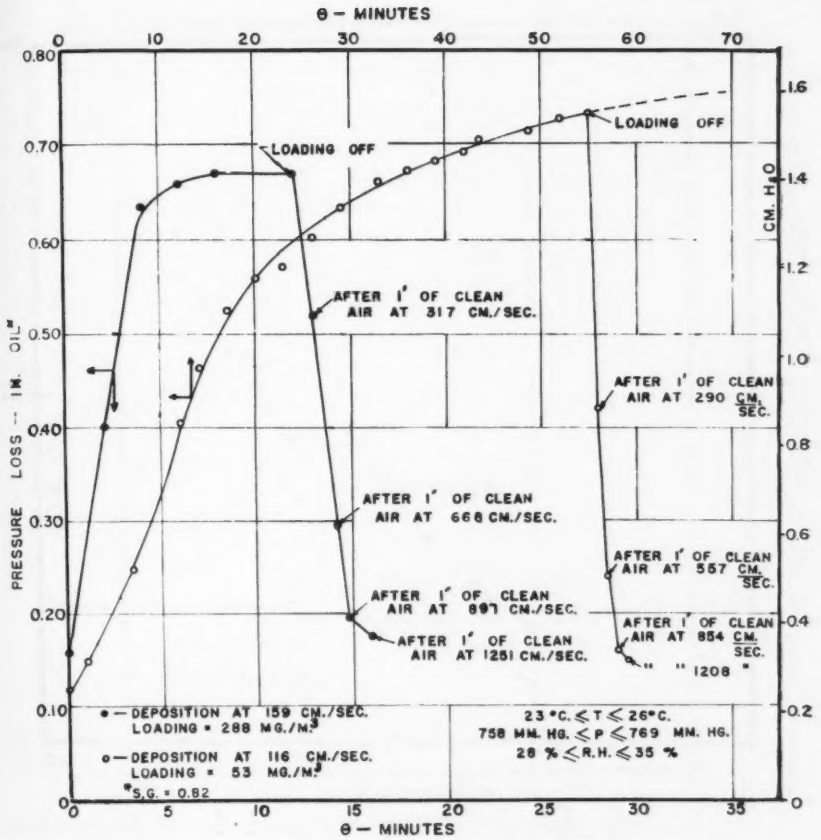

FIGURE 2. Typical pressure loss characteristics of Tyler 100 mesh screen during deposition and removal of dust.

influenced the time required to reach equilibrium pressure loss, but did not alter its final value.

2. Equilibrium pressure loss was not altered if clean air was drawn through the test surface and dust at deposition velocity.

3. If clean air was drawn through the dust laden screen for one minute intervals at velocities greater than that of deposition, a decreased pressure loss was observed across the screen after each interval, until a pressure loss equal to, or very nearly equal to, that of the clean screen was reached.

4. A clean air approach velocity of approximately 1220 cm/sec (40 fps) for one minute reduced pressure loss through the screen to a value close to that of the clean screen for dust deposited at velocities between 116 cm/sec (3.8 fps) and 824 cm/sec (27 fps).

Prediction of Equilibrium Pressure Loss for Single Screen

Figure 3 indicates equilibrium pressure loss through the dust laden screen for runs at dust loadings from 37 to 288 mg/m³ and deposition velocities from 116 cm/sec (3.8 fps) to 824 cm/sec (27 fps). Variations in ambient air quality are noted.

At any duct air velocity the difference between clean screen pressure loss, P_o, and equilibrium pressure loss, P^*, is an indirect measure of dust on the screen. Figure 3 indicates equilibrium pressure loss and clean screen pressure loss for the range of deposition velocities used. It also indicates the following:

1. Dust holding capacity of the screen decreased as deposition velocity increased.

2. At 824 cm/sec (27 fps) approach veloc-

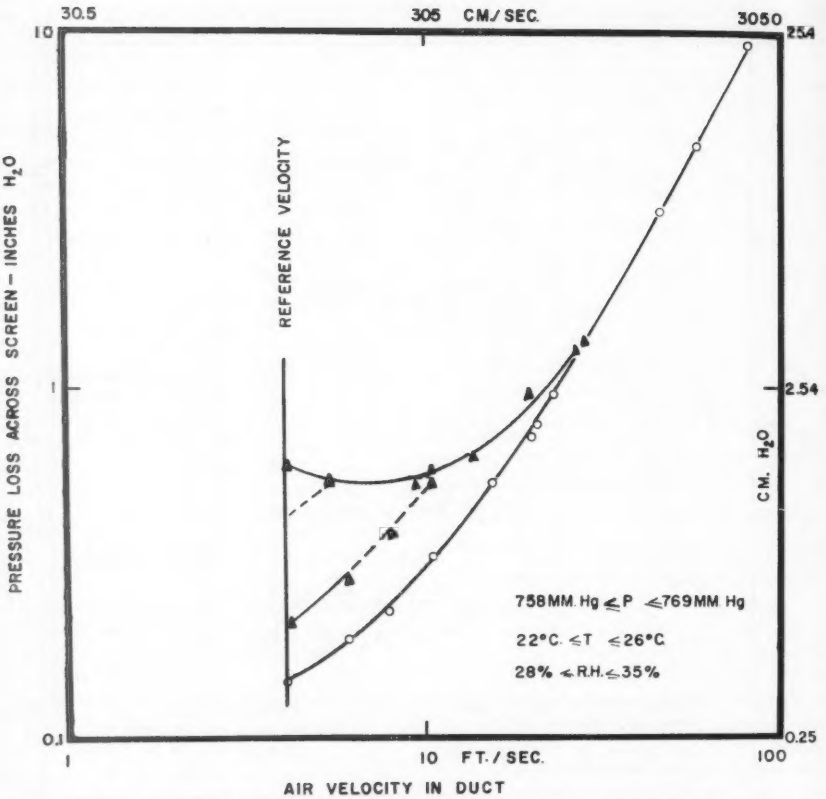

FIGURE 3. Pressure loss through Tyler 100 mesh screen (equilibrium dust laden and clean screen values).

ity, P^* was approximately that of the clean screen, *i.e.* only 0.013 cm H_2O increase. At 824 cm/sec (27 fps) essentially all dust striking the collection surface bounced off or was retained for a short period, agglomerated, and was then re-entrained.

3. Dust loading capacity of the screen, as measured by $P^* - P_o$ was an exponential function of approach velocity and is closely approximated by equation (10) for the velocity range 116 cm/sec (3.8 fps) $< U <$ 732 cm/sec (24 fps).

$$P^* - P_0 = \frac{3.49 \times 10^7}{(U + 214)^3} \qquad (10)$$

where $P^* - P_o$ = screen dust capacity, cm H_2O, as measured at 4.0 fps.

The physical processes of re-entrainment which give rise to an equation of this form are not presently understood. An equation relating $P^* - P_o$ to U^2, which relates to air stream impact pressure was anticipated. Actually, for 3.8 fps $< U <$ 19 fps an equation showing the dependence of $P^* - P_o$ on U^2 does fit the data remarkably well.

4. The clean air approach velocity needed to blow essentially all adhering dust from the screen (approximately 1220 cm/sec (40 fps)) was greater than the velocity at which dust essentially failed to deposit. This suggests that once dust is on the screen it adapts to an aerodynamically stable position.

Interpretation of Re-entrainment Results

P^* and P_o were defined above. P_{no} is now defined as pressure loss through the dust laden screen after one minute application of clean air at velocity *BO*. The following quantities are now defined.

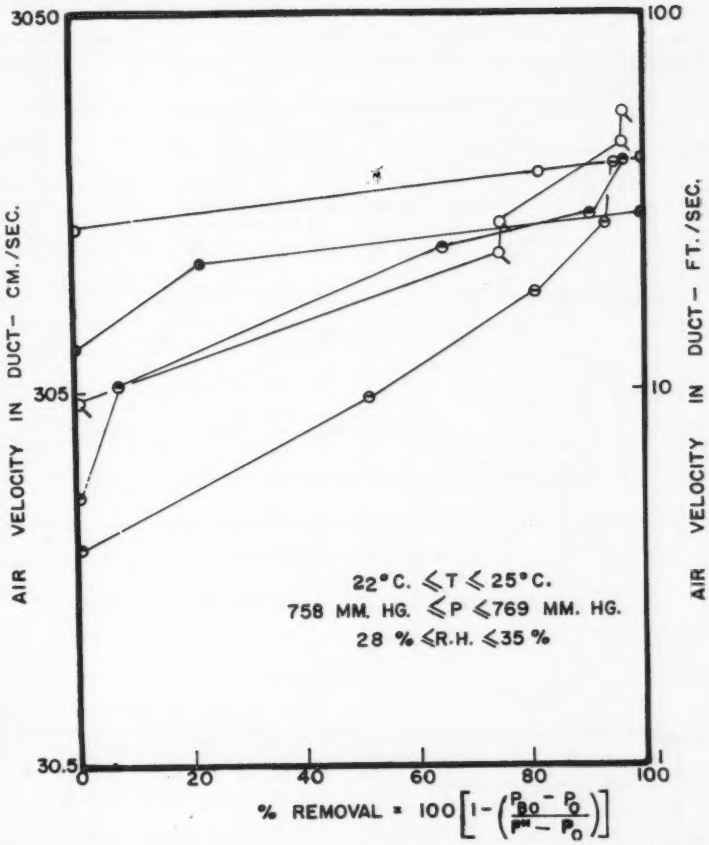

FIGURE 4. Dust removal from single screen after deposition at various velocities.

$$\% \text{ dust on screen} = 100\left(\frac{P_{BO} - P_0}{P^* - P_0}\right) \quad (11)$$

At equilibrium conditions after application of clean air at deposition velocity, $P_{BO} = P^*$ and there is 100% dust on the screen.

$$\% \text{ dust removal} = 100\left[1 - \left(\frac{P_{BO} - P_0}{P^* - P_0}\right)\right] \quad (12)$$

Figure 4 indicates % dust removal from the dust laden screen after one minute screen exposures to various clean air velocities.

If the data of Figure 4 are further treated to reveal relative increase in clean air velocity to effect a given dust removal, an interesting pattern emerges. Thus, in Figure 5 the data are plotted as

$$\frac{U_{BO}}{U(P^* - P_0)}$$

i.e. ratio of blowoff velocity to deposition velocity per unit pressure loss through dust laden screen, vs % dust remaining on the screen as defined above. This treatment shows that when dust is deposited at two velocities a greater relative increase in clean air velocity is required to remove an equal percentage of dust deposited at the high velocity. This treatment is somewhat deceiving, for the total amount of dust involved as the basis for calculation varies with deposition velocity. The qualitative point to be made is one that has long been suspected; dust deposited at high velocities is harder to remove, presumably due to compaction, than dust deposited at low velocities.

If the abscissa of Figure 5 is altered to U_{BO}/U so that blowoff data are not reduced to unit mass of dust (measured by $P^* - P_0$), then the curves of Figure 6 are obtained. These curves are not

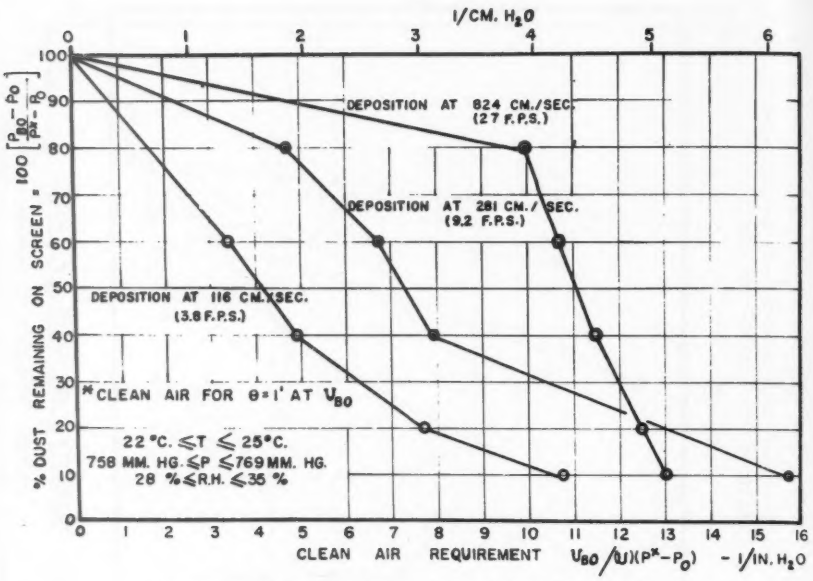
1/CM. H2O
DEPOSITION AT 824 CM./SEC. (27 F.P.S.)
DEPOSITION AT 281 CM./SEC. (9.2 F.P.S.)
DEPOSITION AT 116 CM./SEC. (3.8 F.P.S.)
*CLEAN AIR FOR θ=1' AT U80
22 °C. ≤T ≤ 25°C.
758 MM. HG. ≤P ≤769 MM. HG.
28 %≤R.H. ≤35 %
% DUST REMAINING ON SCREEN = 100 [P80 - P0 / P* - P0]
CLEAN AIR REQUIREMENT U80/U)(P* - P0) - 1/IN. H2O

FIGURE 5. Clean air velocity required for dust removal.

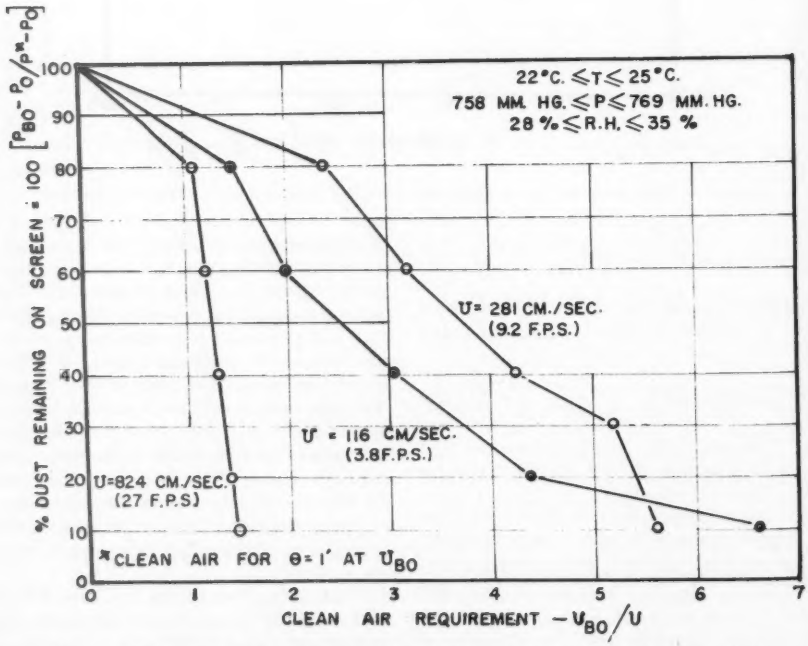
22°C. ≤T≤ 25°C.
758 MM. HG. ≤P≤769 MM. HG.
28 %≤R.H.≤35 %
U= 281 CM./SEC. (9.2 F.P.S.)
U = 116 CM/SEC. (3.8F.P.S.)
U=824 CM./SEC. (27 F.P.S)
*CLEAN AIR FOR θ= 1' AT U80
% DUST REMAINING ON SCREEN = 100 [P80 - P0/P* - P0]
CLEAN AIR REQUIREMENT - U80/U

FIGURE 6. Clean air velocity required for dust removal (reduced abscissa plot).

as revealing as those of Figure 5, but they do indicate dust removal after one minute application of blowoff air.

Particle Size of Re-entrained Dust

Downstream dust samples were obtained during dust deposition and blowoff with clean air. All downstream dust samples were characterized by geometric mean particle sizes (by count) approximately twice that of upstream samples. Downstream dust particle sizes were comparable during collection and blowoff procedures. Calculation of particle number and coagulation rate based on particle proximity in the test duct points to negligible agglomeration and therefore it is concluded that the Tyler screen acted as a particle agglomerator in these tests. These tests confirm the suggestion of E. Anderson[26] that filters should act as particle agglomerators, with larger particles re-entrained downstream of the filter than those impinging on the upstream filter face. Billings, *et al.*[25] also observed agglomeration of iron oxide particles blown off a slag wool filter by shock waves.

Multiple Screen Tests

Tests were performed with three surfaces of Tyler 100 mesh screen separated by edge gaskets of 0.038 cm thick Neoprene rubber. A representative pressure loss-time curve for these tests is shown in Figure 7. The tri-screen appeared to reach equilibrium pressure losses at levels approximately fifteen times greater than that of the single screen. Thus, at 320 cm/sec (10.5 fps) the latter equilibrated at 1.4 cm H_2O as contrasted to 18.3 cm H_2O for the tri-screen assembly. This difference in behavior was found to be due to accumulation of dust between

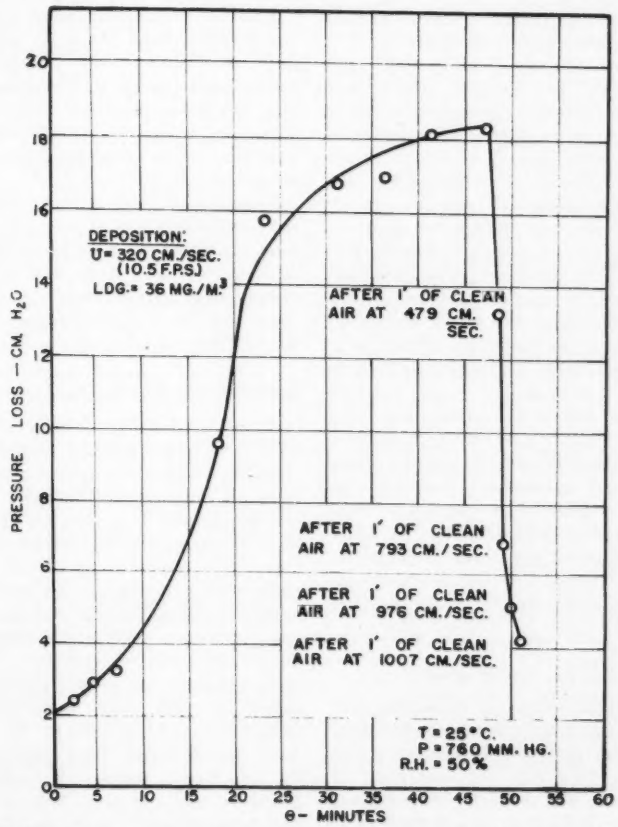

FIGURE 7. Typical pressure loss characteristics of tri-screen assembly during dust deposition and removal.

TABLE I

Air Drag on a Ten Micron Sphere Residing on a Circular Cylinder*

U = 824 cm/sec (27 fps)
T = 25°C
P = 760 mm Hq

θ from stagnation point	Air Drag (dynes)
0°	0
10°	0
20°	5.7×10^{-4}
30°	1.6×10^{-3}
40°	3.1×10^{-3}
50°	4.1×10^{-3}
60°	4.7×10^{-3}
70°	5.1×10^{-3}
80°	5.0×10^{-3}
90°	Region of boundary layer separation

* Assumptions as stated in text.

screens composing the tri-screen assembly, with the largest accumulation between upstream first and second screens. Figure 7 also shows that clean air more effectively removed dust from a single screen than from three screens in series.

Tri-screen operation is more representative of fabric filtration than single screen tests. Dust blown off a single screen is re-entrained in the air stream, but dust removed from all but the downstream surface if a multiple surface assembly has opportunity to strike remaining surfaces before becoming permanently re-entrained. It is postulated that during this process of "accommodation" individual dust particles or agglomerates reach aerodynamically stable positions on the screen matrix. The relative ease with which particles were removed from a single screen leads to the further postulation that particles fail to be re-entrained in high velocity filters because of fluid velocity profile distortion and not because of enormous adhesion forces. The forces are smaller than previously supposed.[17, 18, 27] Particles accommodate to aerodynamically stable positions in the filter matrix where fluid velocities are low. Further, more extensive work is obviously needed to substantiate this suggestion.

Particle Adhesion Force vs Air Drag

Individual particle adhesion measurements[24] indicated that a force of approximately 10^{-3} dyne held a one micron quartz sphere to the test screen. The test dust was not composed of spheres but air drag was nevertheless compared to this force: deviations from sphericity lead to greater particle-surface contact and higher adhesion.

Air drag for a one micron sphere was calculated as outlined above, based on air duct velocity of 824 cm/sec (27 fps), the velocity at which dust essentially failed to deposit on the test screen. Screen approach air velocity was corrected to obtain velocity through the clean screen. This correction favors re-entrainment, for it represents the maximum air velocity attained (90° from forward stagnation point of each cylindrical fiber) as air passes through the clean screen. In this manner, drag forces of less than 10^{-4} dyne were obtained for all locations on a circular cylinder from the forward stagnation point up to separation of the boundary layer at approximately 90°. Therefore, the simple model used to calculate air drag failed to predict by a factor of ten, re-entrainment at the test condition where dust, as measured by screen pressure loss, essentially failed to be retained on the Tyler screen.

Similar calculations were performed for a ten micron sphere (Table I) where an adhesive force of 10^{-2} dyne held particles to surfaces. Again, re-entrainment would not be predicted, but experience indicates that larger particles would be easier to remove than the smaller particles, which were re-entrained at this test condition.

Therefore, it was concluded that other factors, not incorporated in the simple model used for calculation of air flow, must influence the re-entrainment mechanism. Included among these variables are particle inertia and boundary layer distortion by lodged particles and adjoining screen fibers.

Summary and Conclusions

At ambient air conditions of approximately 25°C and 30% relative humidity, essentially complete removal of approximately one micron silica particles lodged on a Tyler 100 mesh woven screen occurred at a clean air approach velocity of 1220 cm/sec (40 fps), which corresponds to a velocity of 4013 cm/sec (132 fps) through the clean screen. Essentially no dust deposition occurred at 824 cm/sec (27 fps) approach velocity.

Experiments with a tri-screen assembly of Tyler 100 mesh screen were characterized by dust accumulation between screens, high pressure loss, and poor dust removal by high velocity air. Therefore, it is suggested that dust retention on filter surfaces is not due to enormous forces of adhesion between particles and surface, but to distortion of the fluid velocity profile in the filter matrix, which leaves particles in aerodynamically stable positions.

During dust deposition and blowoff procedures with clean air, particles downstream of the collector were significantly larger than upstream particles. The Tyler screen collector acted as a particle agglomerator.

A simple model utilizing potential flow theory was used to calculate air drag acting on particles immersed in the boundary layer on cylindrical fibers comprising the collector. For a specific flow condition, air-drag calculated in this manner was lower, by a factor of ten, than particle to surface adhesion force determined in a companion study. Particles should not have been re-entrained. Other factors, not accounted for in the assumed flow model, obviously greatly influenced the re-entrainment process.

Nomenclature

C_D = Drag coefficient, dimensionless
D_P = particle diameter, cm.
F_D = Drag force, dynes
P = Static pressure, dynes/cm^2
P_o = Pressure loss through clean screen, cm H_2O
P^* = Equilibrium pressure loss through dust laden screen, cm H_2O
P_{BO} = Pressure loss through dust laden screen after 1′ of clean air at velocity BO, cm H_2O
u = Average fluid velocity in x direction, cm/sec.
u^* = Fluid velocity at edge of laminar-sublayer, cm/sec.
U = Average duct air velocity upstream of collector screen, cm/sec.
U_{BO} = Average duct air velocity to blow dust off collector screen, cm/sec.
v = Average air velocity in y direction, cm/sec.
ρ = Density of air, g/cm^3.
μ = Viscosity of air, cp.

References

1. Albrecht, F.: Theoretical Investigations of Dust Deposition from Flowing Air and Its Application to the Theory of the Dust Filter. *Physik. Z. 32:* 48 (1931). Tech. Rpt. No. 3: Univ. Ill., Urbana (1951). Transl. by P. J. Domotor.
2. Chen, C. Y.: Filtration of Aerosols by Fibrous Media. *Chem. Rev. 55:* 595 (1955).
3. Ranz, W. E.: *The Impaction of Aerosol Particles on Cylindrical and Spherical Collectors.* Tech. Rpt. No. 3: Univ. Ill., Urbana (1953).
4. Ranz, W. E.: *The Role of Particle Diffusion and Interception in Aerosol Filtration.* Tech. Rpt. No. 3: Univ. Ill., Urbana (1953).
5. Rodebush, W. H., I. Langmuir, and V. K. La Mer: *Filtration of Aerosols and the Development of Filter Materials.* O.S.R.D. No. 865, (Sept. 1942).
6. Sell, W.: Dust Precipitation on Simple Bodies and in Air Filters. *Forsch. Gebiete Ingen. 2:* 347 (1941). Tech. Rpt. No. 3: Univ. Ill., Urbana (1951). Transl. by P. J. Domotor.
7. Stairmand, C. J.: Dust Collection by Impingement and Diffusion. *Trans. Inst. Chem. Engrs. (London) 28:* 130 (1950).
8. Ramskill, E. A., and C. L. Anderson: The Inertial Mechanism in the Mechanical Filtration of Aerosols. *Coll. Sci. 6:* 416 (1951).
9. Gillespie, T., and E. Rideal: On the Adhesion of Drops and Particles at Solid Surfaces. I. *J. Coll. Sci. 10:* 265 (1955).
10. Gillespie, T., and E. Rideal: On the Adhesion of Drops and Particles at Solid Surfaces. II. *J. Coll. Sci. 10:* 281 (1955).
11. Gallily, I., and V. K. La Mer: On the Behavior of Liquid Droplets After Impinging on Solid Surfaces. *J. Phys. Chem. 62:* 1295 (1958).
12. Lapple, C. E., R. J. Stasny, and T. E. Wright: *High Velocity Filters.* Tech. Rpt. 55-437. Wright-Paterson Air Force Base, Ohio (Oct. 1957). A.S.T.I.A. Doc. No. AD-142075.
13. Billings, C. E., and L. Silverman: Low Cost Cupola Dust Collector. *Air Eng. 1:* 44 (1959).
14. Bagnold, R. A.: *The Re-entrainment of Blown Sand and Desert Dunes.* Methuen and Co., Ltd., London (1954).
15. Gutterman, B., and W. E. Ranz: Dust Properties and Dust Collection. *Proc. A.S.C.E., J. San. Eng. Div.:* 25 (July, 1959).
16. Rumpf, H.: Uber das Ansetzen Fein Verteiler Stoffe an den Wanden von Stromungskanalen. *Chemie. Ing. Tech. 25:* 217 (1953).
17. Kordecki, M. C., and C. Orr: Adhesion of Solid Particles to Solid Surfaces. *Arch. Env. Health. 1:* 13 (July, 1960).
18. Corn, M.: The Adhesion of Solid Particles to Solid Surfaces. II. Paper # 61-11, A.P.C.A. Mtg., New York, N.Y. (June, 1961).
19. Lamb, H.: *Hydrodynamics.* 6th Ed., p. 687, Dover Pub. Co., New York, N. Y. (1932).
20. Meksyn, D.: The Laminar Boundary Layer Equations. *Proc. Roy. Soc. (London). 192A:* 545 (1948).
21. Knudsen, J. G., and D. L. Katz: *Fluid Dynamics and Heat Transfer.* p. 288, McGraw-Hill Book Co., New York, N. Y. (1958).
22. Silverman, L.: Experimental Test Methods. *Air Pollution Handbook.* Magill, P. L., F. R. Holden and C. Ackley, Eds. pp. 12-19, McGraw-Hill Book Co., New York, N. Y. (1956).
23. Wright, B. M.: A New Dust Feed Mechanism. *J. Sci. Instr. 27:* 12 (1950).
24. Anderson, D. M.: *Mechanisms in Electrostatic Filtration of Aerosols with Fixed and Fluidized Granules.* Ph.D. Thesis. Harvard University (1958).
25. Billings, C. E., L. Silverman, R. Dennis, and L. Levenbaum: Shock Wave Cleaning of Air Filters. *J. Air Poll. Control Assn. 10:* 318 (1960).
26. Anderson, E.: Separation of Dust and Mist. *Chemical Engineers' Handbook,* J. H. Perry, Ed., p. 1345, McGraw-Hill Book Co., New York, N. Y. (1934).
27. Corn, M.: *The Adhesion of Solid Particles to Solid Surfaces.* Ph.D. Thesis. Harvard University (Jan. 1961).

A Compact Cascade Impactor for Field Survey Sampling

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A new design for a cascade impactor is presented. Particulate material is collected at four impaction stages on two standard 1″ x 3″ glass microscope slides, with two deposits on each slide. The deposits can be spread out during collection by using an external slide movement mechanism. A 1″ diameter filter follows the impaction stages. A calibration nomograph is presented. Results obtained using this calibration are in good agreement with the results obtained by direct sizing of simultaneously drawn membrane filter samples.

Introduction

THE use of cascade impactors for particle size analysis was reviewed in a previous paper.[1] It was shown that cascade impactor analysis has many significant advantages over other methods. The major disadvantages were not fundamental to the method but due to a lack of suitable instruments. Modifications of existing commercial equipment, such as those of K. R. May,[2] the Los Alamos Scientific Laboratory,[3] and the Health and Safety Laboratory[1] (HASL), made them usable in the field, but fell short of making them convenient or reliable. It was concluded that cascade impactor analysis would not be a convenient field method until an instrument was designed specifically for field sampling. A development project was initiated and resulted in the cascade impactor illustrated in Figure 1.

Design Objectives

The primary objective was a compact unit which could:

(1) be conveniently used for large scale sampling programs under industrial conditions,
(2) withstand rugged field use and abuse without damage,
(3) take sufficient sample to permit accurate mass analyses on all of its stages,
(4) collect all particles below 25 microns,
(5) permit easy loading and unloading of collecting slides, and
(6) be cleaned efficiently in the laboratory or in the field.

Description of Instrument

The over-all dimensions are 1⅜″ × 1½″ × 6″, which includes a 1⅛″ diameter filter holder and slide movement mechanism. The total weight is ten ounces. The impaction surfaces are standard 1″ × 3″ glass microscope slides coated with an adhesive layer of silicone grease. The grease serves two functions: first, it is essential for the efficient collection of dry particles, and second, it seals the slide to the body of the impactor, preventing air leakage.

Figure 2 shows a section view of the instrument illustrating the air path. The jet dimensions for the four impaction stages are listed in Table I. After passing the fourth jet, the air is drawn through an efficient filter. The lower end of the cascade impactor body is designed with an O-ring seal and fits into the inlet of the standard HASL 1⅛″ filter head.

The success of this design depends upon the maintenance of close tolerances in the machining of the jets, and in the very flat, smooth surface upon which the collecting slides rest and seal against. The instrument is machined from aluminum, providing the necessary rigidity without excessive weight. All surfaces are smooth and dead air spaces are minimized.

A special feature is the manual slide movement mechanism. It consists of a thin plate with four arms which position the slides and guide their movement. The arms are spring-loaded and have two rest positions. In the upper part of Figure 1 they are shown closed and in the lower part they are open. The slides can be advanced as the sampling proceeds without disturbing the integrity of the air path seal. Movement is in 1/16″ increments over a total travel of ½″, permitting the collection of up to nine times more sample than can be collected on a non-moving slide. Thus, there is a much greater likelihood of collecting enough sample on stages 3 and 4 for analysis without overloading the adhesive at those positions. The notches and spring-loaded

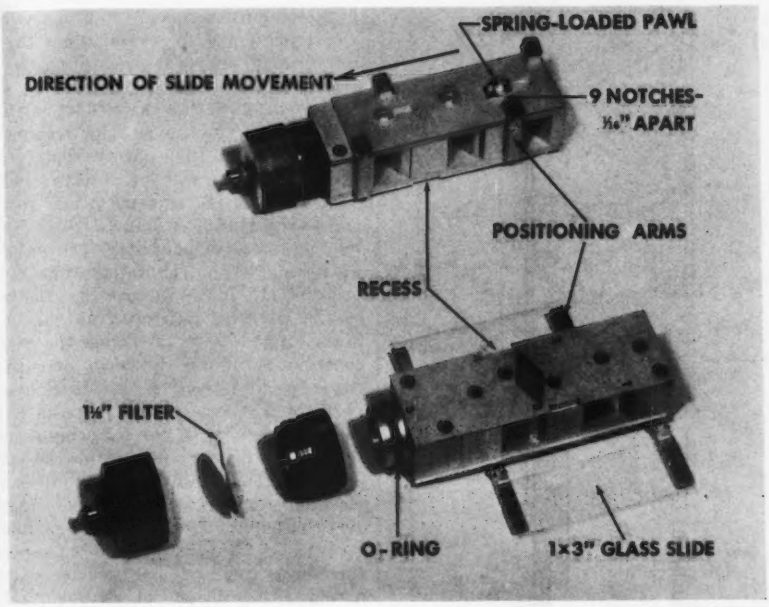

FIGURE 1. HASL cascade impactor. Upper view shows adhesive coated glass microscope slides and 1⅛" diameter filter holder in place. Lower view shows the opposite side of the instrument with the arms of the slide movement mechanism in the open position and the filter head detached.

pawl of the mechanism permit slide movement in one direction only, preventing inadvertent smearing of the collected material.

Calibration

The instrument was calibrated empirically by direct microscopic sizing of particles collected on each impaction stage. The procedure was the same as that used by the HASL in calibrating the Casella cascade impactor.[1] The Casella instrument was calibrated at one flow rate only (17 liters/min), while the HASL cascade impactor was calibrated over a range of flow rates to permit greater latitude in size measurement. As a result, considerably more microscopic sizing was necessary for this calibration.

A generalized calibration was developed which is applicable to dusts with densities between 0.8 and 20 grams/cm^3 and for any sampling flow rate between 2 and 40 liters/minute. This calibration is illustrated by the nomogram of Figure 3, which is based on the following equations:

$$\rho V^{1.5} d^2 = 2820$$

$$Q = 6VS$$

where: ρ = particle density—grams/cc
V = jet velocity—meters/second
d = particle diameter—microns
Q = sampling flow rate—liters/minute
S = jet cross-sectional area—square centimeters

The accuracy of the calibration was checked by comparing cascade impactor sample results with size analyses performed on simultaneously drawn membrane filter samples. The results from five such tests, each performed at a different sampling rate, are shown in Table II. The agreement, for both median size and standard deviation, seems excellent. The size distribution curves for the 4.8 liter/minute test are illustrated in Figure 4.

Secondary Deposition and Wall Losses

Figure 5 shows collecting slides with U_3O_8 deposits on them. The slides on the right show nine separate traces per stage, obtained by advancing the slide during collection. The slides on the left show single trace deposits. These slides were permitted to collect more material than is desirable in order to illustrate the appearance of the deposit. When deposits approach these

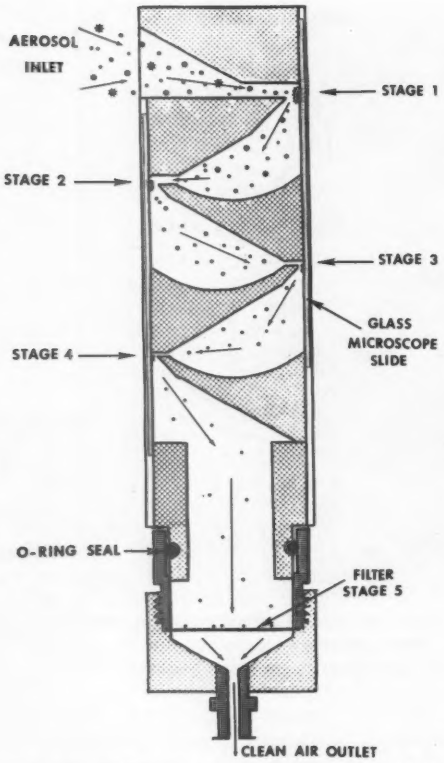

FIGURE 2. Pictorial cross-sectional view of the instrument while sampling. The particle size is grossly exaggerated.

densities, secondary deposition, wall losses, and slippage of particles to succeeding stages becomes excessive.

Secondary deposition may be noted on stages 1 and 2. This deposition takes place on the collecting surface at points distant from the primary deposit. The slides are usually free of particles downstream of the primary deposit for a distance equal to several times the width of the primary deposit. Deposition beyond this "clean" area is most likely due to diffusional deposition, since these areas have relatively low-velocity air movement. The amount of such secondary deposition varies slightly with the over-all sampling rate but is relatively low under all conditions. It is usually less for stages 3 and 4 than for stages 1 and 2. Secondary deposition expressed in percentage of total deposition for a number of calibration runs is indicated in Table III. It can be seen that the percentage of the particles depositing in this manner is in the range 13% to 25%, while the relative mass contribution of this secondary deposition varies from 5% to 11%. The size distribution of the particles in the secondary deposit is closer to the size deposited at the following stage than to that of the primary deposit on the same stage. The same mechanism that deposits particles as secondary deposition on the slide undoubtedly also causes some particles to deposit along the walls of the air path near the same points. This contributes to "wall losses," *i.e.*, material adhering to the walls of the instrument rather than the collecting surfaces.

To investigate the magnitude of these "wall losses," a number of tests were performed. All the material remaining in the impactor was removed, transferred to a membrane filter, and analyzed in the same manner as the material deposited on each stage. Table II shows some of the results found. These are conservative figures which overestimate the true "wall loss" since they include material deposited on the outside surfaces of the impactor during sample collection, as well as some of the secondary deposition from the slides which scraped off as the slide was advanced. Nevertheless, the fraction of the material in a sample which ends up on the walls instead of on collecting surfaces does not exceed 30%. While any loss is undesirable and detracts from the sampler efficiency as a total collection

TABLE I

Impaction Stage Characteristics

Stage Number	Jet Dimensions inches	Jet Cross-Sectional Area		Jet Velocity	
		square feet	square centimeters	feet/second	meters/second
1	0.140 × 0.785	765×10^{-6}	710×10^{-3}	$21.8\ Q_C$*	$0.235\ Q_L$**
2	0.060 × 0.785	327×10^{-6}	304×10^{-3}	$51.0\ Q_C$	$0.548\ Q_L$
3	0.025 × 0.785	136×10^{-6}	127×10^{-3}	$122\ Q_C$	$1.31\ Q_L$
4	0.010 × 0.785	54.5×10^{-6}	50.6×10^{-3}	$306\ Q_C$	$3.30\ Q_L$

* Q_C = Sampling rate in cubic feet/minute

** Q_L = Sampling rate in liters/minute

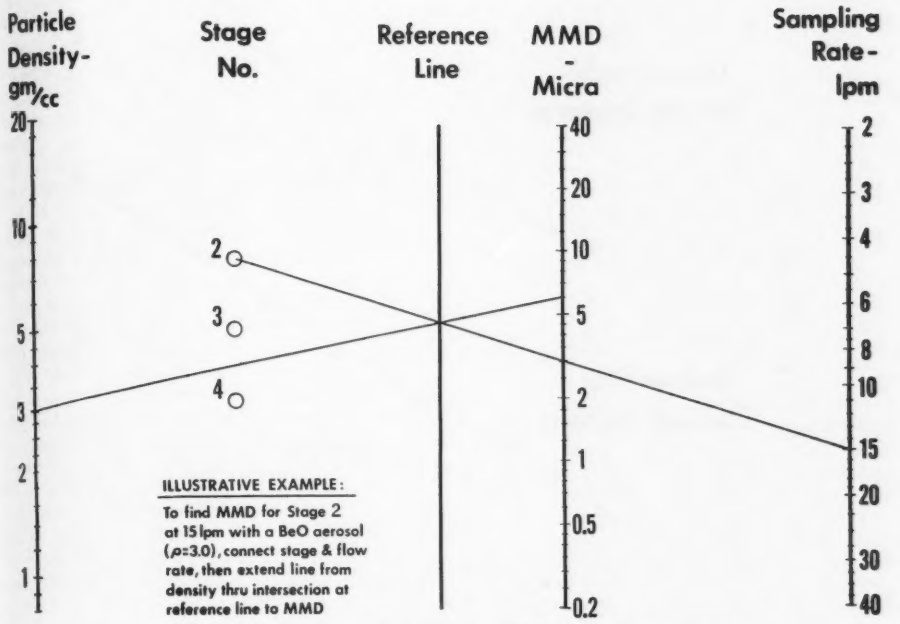

FIGURE 3. Calibration nomogram for HASL cascade impactor.

device, it does not materially affect its use to obtain particle size distribution data. The results shown in Table II indicate that despite the losses, the relative proportions collected on the impaction stages, when plotted against the stage calibration values, provide a reasonably accurate estimate of over-all particle size distribution in the dust.

Use of the Cascade Impactor

Preparation of Slides

The slides must be coated with a non-drying adhesive layer. The HASL uses Dow Corning 200 Fluid (Dow Corning Corp., Midland, Michigan) with a viscosity of 60,000 centistokes. Several drops are placed on the surface of a slide and spread into a thin film with the short edge of a second glass slide. This provides an efficient adhesive coating for collecting the dust and sealing the air path. The amount of material applied should not be so great as to run under the collecting surface when the slide is pressed into position.

The pre-coated slides are placed in the uppermost position for collecting the sample and may then be moved during the sampling period to collect a maximum amount of sample without overloading the slides. The HASL finds it convenient to pre-score the glass slides at the center with a diamond point stylus. After collection of the sample, the slides can be readily parted to facilitate analysis of the separate stages. The parting of the slide may be done either immediately after collection, or at a later time in the laboratory, whichever is most convenient. If standard microscope slide holders are used to transport the samples, it will probably be most

TABLE II

Results of Simultaneous Membrane Filter and Cascade Impactor Samples

Sampling Rate-lpm	Membrane filter			Cascade Impactor		
	Median Particle Diameter Mg-μ	Geometric Standard Deviation σ	Mass* Median Diameter M′g-μ	Mass Median Diameter M′g-μ	Geometric Standard Deviation σ	"Wall Loss" % of Total Sample's Mass
4.8	0.66	2.2	4.0	4.2	2.2	27
10.0	0.70	2.1	3.4	3.7	2.3	19
13.0	0.94	2.0	3.6	3.0	1.9	29
17.5	0.74	2.0	3.1	3.0	2.1	26
23.0	0.72	2.1	3.6	3.4	2.1	27

* Mass median diameter calculated by formula of Hatch and Choate: $\log M'g = \log Mg + 6.9 \log^2\sigma$.

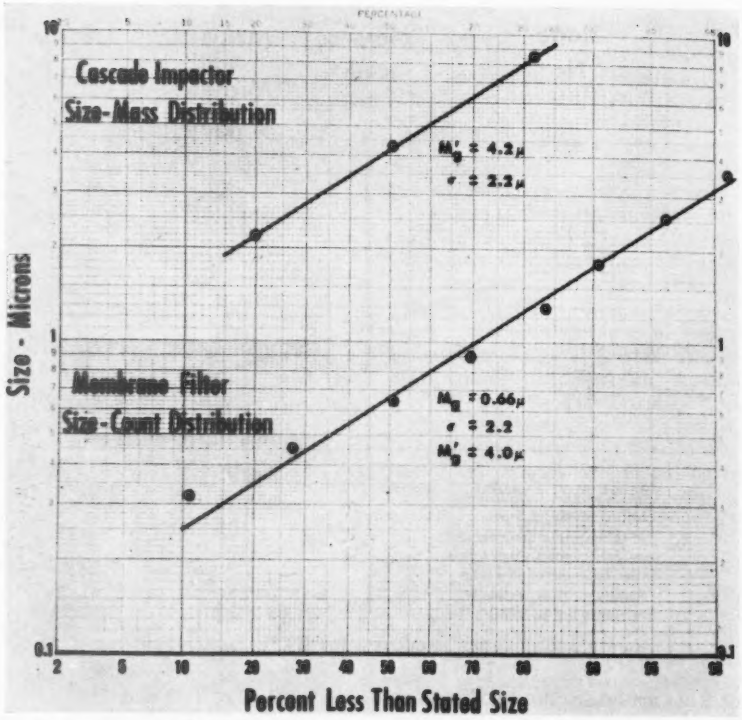

FIGURE 4. Results of calibration check at a sampling rate of 4.8 liters/min. The upper curve represents size-mass distribution and is obtained by plotting the mass distribution data from the cascade impactor stages against stage MMD values derived from Figure 3. The lower curve is a particle size distribution plot obtained by direct microscopic sizing of simultaneous membrane filter samples.

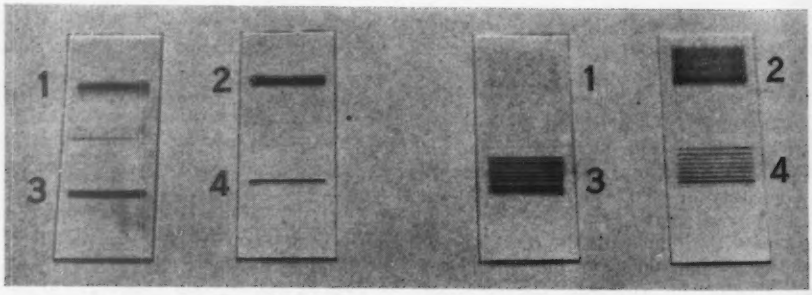

FIGURE 5. Collecting slides showing the appearance of the deposited material. On the left are single trace deposits. On the right, multiple deposits are shown, obtained by using the slide movement mechanism.

convenient to break the slides in the laboratory just prior to analysis.

Unless extremely heavy samples are collected, it is usually not necessary to clean the cascade impactor after every sample collection. The small amount of material which adheres to the walls is not readily re-entrained during a subsequent sample collection.

Sample Collection

After the adhesive coated slides and filter are placed in position, the cascade impactor is ready for sampling. Any convenient suction source may be used to move the air, provided it can operate at the desired sampling rate. It is important that the flow rate be metered accurately since the stage calibration values vary with flow rate. If an in-line flowmeter, such as a rotameter, is used downstream of the cascade impactor, a suitable pressure correction must be applied to the flowmeter reading. The head loss across the impactor will vary with the sampling rate and the resistance of the filter used as the fifth stage.

The slides should be advanced as soon as a visible deposit can be observed. This will usually take no more than two to five minutes, even in a relatively clean atmosphere. To advance the slides, slowly push the knob in the center of the slide movement mechanism until the pawl clicks into the second position. Repeat this procedure as many times as required to obtain the desired quantity of sample up to the maximum movement of eight increments. Lift the arms of the slide holder until they lock in the up position. The slides may be pried up by inserting the point of a pocket knife or pair of tweezers into the recess cut into the center of the bearing surface on each side. Lift the slides away carefully to avoid smearing the deposited dust and place them in the slide holders for transport to the analytical laboratory.

Cleaning

When Dow Corning 200 Fluid is used as an adhesive on the slides, the impactor should be washed with a suitable solvent such as benzol or one of its homologs. It should then be rinsed with clean solvent from a wash bottle and air dried. If any material remains, it can usually be removed by washing with a detergent solution, using a small brush in the recesses. This treatment should suffice since all surfaces are visible and accessible.

Summary and Conclusions

A cascade impactor designed for efficient field survey sampling has been described. It has been found suitable for the rough estimation of particle size distribution of airborne materials commonly encountered in industry. By appropriate choice of sampling flow rate and the use of the manual slide movement mechanism, it is possible to collect samples which will provide reliable particle size estimates under almost all operating conditions. Because of the relatively small size of the instrument and the ease of sample handling, large numbers of samples can be taken in a reasonably short period of time.

A generalized calibration is presented for analysis of collected samples. It is applicable to dusts of any density whose shape is relatively regular. It is anticipated that with the availability of this instrument, much more size information will be collected in future operations of the Health and Safety Laboratory.

TABLE III

Secondary Deposition on Slides

Stage Number	No. of Tests	Per cent of Particles			Per cent of Mass*		
		Max.	Min.	Average	Max.	Min.	Average
1	3	36	19	25	13	3	6
2	10	28	12	20	18	6	11
3	7	27	3	14	12	1	6
4	6	20	6	13	8	2	5

* Calculated from particle size data by formula:

$$\sum N_T d^3 - \sum N_s d^3,$$

where N_T = total number of particles — primary and secondary, N_s = total number of particles, secondary.

Acknowledgments

Grateful acknowledgement is hereby made to Philip Rogal who performed most of the optical microscopic sizing upon which the calibration is based, and to Union Industrial Equipment Company, Inc. of Port Chester, New York, who fabricated the prototype and production versions of the HASL cascade impactor.

References

1. LIPPMANN, M.: Review of Cascade Impactors for Particle Size Analysis and a New Calibration For the Casella Cascade Impactor. *Am. Ind. Hyg. Assoc. J. 20:* 406 (Oct. 1959).
2. MAY, K. R.: A Cascade Impactor With Moving Slides. *AMA Arch. of Ind. Health 13:* 481 (May 1956).
3. LASL: Modification of the Casella Impactor, in *Encyclopedia of Instrumentation for Industrial Hygiene*, edited by Yaffe, C. D., D. H. Byers, and A. D. Hosey, pp. 142-4, Univ. of Michigan, Ann Arbor, Michigan (1956).

The Toxicity of Vinyl Chloride as Determined by Repeated Exposure of Laboratory Animals

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Groups of laboratory animals were exposed repeatedly for up to six months to either 500, 200, 100 or 50 ppm vinyl chloride in air. Detectable changes occurred at all but the lowest concentration. The results are discussed and handling precautions suggested.

Introduction

VINYL chloride (CH_2=$CHCl$) is a chemical of great industrial importance. It is used in the preparation of polyvinyl chloride resin, as a copolymer in saran and other plastics, as a chemical intermediate and as a solvent. Because of the flammability of vinyl chloride, it has been generally assumed that the greatest hazard associated with vinyl chloride is that due to its flammability rather than its toxicity.[1]

The toxicity of vinyl chloride has been reviewed by von Oettingen[2] and more recently by Mastromatteo *et al.*[3] von Oettingen concluded that the gas was anesthetic in high concentrations and that considerable interest had been shown in the use of vinyl chloride as a surgical anesthetic. However, its effect on the circulatory system has discouraged exploitation of this property. No doubt the hazard from flammability has also hindered this use. Only limited repeated exposures which were reported by Schaumann[4] were discussed by von Oettingen. These repeated exposures indicated little or no chronic effects even from anesthetic concentrations.

Mastromatteo *et al.*[3] also discussed the published data and reported the results of single exposures of mice, rats and guinea pigs which confirmed the low acute toxicity of vinyl chloride. Mastromatteo reported that only two human fatalities due to vinyl chloride had been reported.

It can be concluded from the published toxicological data that anesthesia is the only significant effect of acute exposure. Sufficient repeated exposures have not been reported to draw conclusions about chronic toxicity. The Threshold Limit Value of 500 ppm suggested by the American Conference of Governmental Industrial Hygienists (ACGIH)[5] is reported by Smyth[6] to be based on single animal exposures and human experience.

The following report summarizes the results of repeated exposures of laboratory animals to either 500, 200, 100 or 50 ppm of vinyl chloride. The significance of the results is discussed and recommendations for a threshold limit value are made.

Experimental Procedures

Materials Tested

Vinyl chloride, CH_2=$CHCl$, is a colorless gas. It has a boiling point of −13.35°C (+7.93°F) and a freezing point of −154°C (−244.82°F). The material polymerizes readily and hence is sometimes inhibited with phenol or tertiary butylcatechol. Vinyl chloride is very flammable, its flashpoint being −78°C (−108°F). The explosive limits are from 4% to 22% by volume. It has little odor although high concentrations may smell faintly sweet.

A single, uninhibited sample was used in these studies. It was shown by mass spectrographic analysis to be essentially pure CH_2=$CHCl$, air being the only impurity detected in gas phase samples.

Source and Feeding of Animals

The rats and rabbits used in this study were obtained from the stock colony of this laboratory, the guinea pigs were obtained from a commercial grower[7] and the dogs were purebred beagles obtained from a local kennel. The rats and dogs were fed Purina Laboratory Chow[8] or Famo Laboratory Ration.[9] The rabbits and guinea pigs received Famo Rabbit Breeder Ration. The guinea pig diet was supplemented with carrots.

Experimental Protocol

The experiments were conducted in three phases. In the first phase, groups of 10 male

and 10 female rats were exposed seven hours per day five days per week to 500 ppm for 4.5 months. Exposures were given in a 160-liter chamber previously described.[10] Mortality and growth records were kept. Final organ weights were obtained and tissues were saved for microscopic examination. Five male and five female rats served as unexposed controls.

The second phase consisted of repeated 7-hour daily exposures of 20–24 male and 24 female rats, ten male and eight female guinea pigs, three male and three female rabbits and one male and one female dog to either 200 ppm or 100 ppm of vinyl chloride. These animals and two groups of controls were carefully selected and matched on the basis of age, condition and weight. The first group of controls received no exposure and served as unexposed controls. The second group received repeated daily 7-hour exposures to room air in a chamber similar to the one used for exposures to the chemical. This group is referred to as the air-exposed control group. In addition to the animals receiving 7-hour daily exposures, eight separate groups of five male rats each were exposed to either 200 or 100 ppm for 4, 2, 1 or 0.5 hours per day.

The procedures and equpiment used were basically the same as reported previously.[11] Growth and mortality records were kept on all groups. The livers of the dogs were biopsied prior to exposure and after 3½ months of exposure, hence the liver of each dog served as its own control. Pre-exposure and terminal hematological determinations were made on all dogs and terminal determinations on representative groups of rats. Urine samples were collected from the dogs and representative groups of rats. At the termination of the experiment, part of the rats were starved overnight and then these and all the guinea pigs and rabbits were killed by decapitation on the day after their last exposure. The dogs were killed by exsanguination after anesthesia with thiopental, sodium (Pentothal, Abbott). Samples of blood were taken of representative groups of animals for determination of alkaline phosphatase, serum-urea-nitrogen (SUN), serum-glutamic-pyruvic-transaminase (SGPT), and serum-glutamic-oxalacetic-transaminase (SGOT). The organs were weighed and tissues fixed for histopathological examination. The rats which were not killed the day after exposures were stopped were pastured for eight weeks and then sacrificed in the previously described manner.

The third phase of this experiment consisted of repeated daily 7-hour exposures of 24 male and 24 female rats, 12 male and 12 female guinea pigs, 3 male and 3 female rabbits and one male and one female dog to 50 ppm vinyl chloride. Equal matched groups served as unexposed and air-exposed controls. Three additional groups of 10 male rats each were exposed for 4, 2 or 1 hour per day to 50 ppm.

The procedures followed were essentially the same as used for exposures to 200 and 100 ppm except that hematological examinations were made on the dogs after three months and liver biopsies were made only prior to exposure. Urine was collected from the rabbits as well as the rats and dogs. The rats which were not sacrificed at the end of the exposures were pastured for six weeks and then sacrificed.

Equipment Used

The exposure equipment used has been described previously.[11] However, in order to gain additional data about the results of repeated short daily exposures, it was necessary to devise a method of introducing additional groups of rats. This was done without opening the doors of the chamber by dropping the rats through chutes made of 3.25-inch stainless steel tubing. These chutes were closed with a rubber stopper except during the brief time it took to insert the rats. The chutes, which were sloped at a 45° angle, ended in covered, screened cages inside the chamber. The additional groups were started 3, 5, 6 and 6.5 hours after the 7-hour exposures started. Since all animals were removed after the 7-hour exposure was completed, this routine resulted in exposures lasting 4, 2, 1 or 0.5 hours.

The vinyl chloride was metered from a saran plastic bag which served as a reservoir for the gas. Metering of the gas was done by Dual Syringe Pumps.[12] Total air flow through the chambers was measured by means of calibrated flow meters.

Analysis of the Chamber Atmospheres

Analyses of the air were made by direct combustion of a known volume of air in a heated quartz tube. The resulting chloride was trapped in 1% sodium formate—1% sodium carbonate solution and subsequently titrated by a micro-Volhard technique. The results of the individual analyses were within 15% of the theoretical concentrations during the exposures to 200, 100 and 50 ppm. The average concentrations recovered were 197, 100.5 and 48.7 ppm respectively.

Results of Repeated Exposures

Exposure to 500 ppm Vinyl Chloride

The rats exposed repeatedly at 500 ppm for 4.5 months, grew normally and no changes were

TABLE I

Summary of Terminal Average Body and Organ Weights of Male Rats Receiving Repeated Exposures to Vinyl Chloride 5 Days per Week

Concentration in ppm	Months on Exposure	Duration of Daily Exposure, hours	Ratio of Survival	Final Average Body Weight, g	Organ Weights, g/100 g Body Weight					
					Lung	Heart	Liver	Kidney	Spleen	Testes
Unexposed control	0	0	4/5	304	0.54	0.33	2.52	0.71	0.15	0.89
500	4.5	7	7/10	312	0.56	0.33	3.00[a]	0.73	0.17	0.95
Unexposed control	0	0	11/12	343	0.53	0.32	2.45	0.69	0.14	0.80
Air exposed control	6	7	10/12	356	0.52	0.32	2.52	0.70	0.15	0.76
200	6	7	9/12	341	0.52	0.32	2.85[b]	0.68	0.17	0.94
200	6	4	4/5	349	0.47	0.29	2.66[c]	0.64	0.16	0.85
200	6	2	4/5	341	0.56	0.30	2.62[d]	0.64	0.16	0.89
200	6	1	3/5	350	0.48	0.28	2.46	0.61	0.13	0.78
200	6	0.5	4/5	339	0.51	0.29	2.38	0.67	0.14	0.95
100	6	7	7/12	352	0.51	0.29	2.61[e]	0.63	0.15	0.85
100	6	4	3/5	360	0.51	0.28	2.62	0.65	0.15	0.74
100	6	2	4/5	331	0.53	0.31	2.64	0.67	0.16	0.93
100	6	1	3/5	387	0.49	0.28	2.52	0.64	0.15	0.78
100	6	0.5	5/5	363	0.45	0.30	2.42	0.64	0.16	0.78
Unexposed* control	0	0	10/12	354	0.49	0.31	2.43	0.64	0.14	0.84
Air exposed* control	6	7	8/12	393	0.59	0.30	2.41	0.63	0.15	0.78
200*	6	7	8/8	385	0.47	0.29	2.59[e]	0.64	0.15	0.71
100*	6	7	6/7	376	0.47	0.31	2.53[f]	0.65	0.14	0.76

* Pastured for 8 weeks after exposures ceased.

(a) P = 0.001
(b) P = <0.001
(c) P = 0.07
(d) P = 0.1
(e) P = 0.02
(f) P = 0.13

apparent grossly at autopsy. Microscopically their livers showed increased central lobular granular degeneration and the kidneys showed interstitial and tubular changes. The average weight increase of the livers of the male rats was statistically significant (P = 0.001), Table I. The average weight of the livers of the female rats was above that of the controls but not statistically significant, Table II. SUN, SGPT, S-GOT, and alkaline phosphatase determinations were within normal limits (Table III).

Exposure to 200 ppm Vinyl Chloride

All groups exposed seven hours per day 138–144 times in 204 days were normal in appearance, mortality and growth. Hematological, SUN, S-GOT, SGPT and alkaline phosphatase values (Table III) and the results of the urinalysis were within normal limits. Gross pathology was normal in all species. Micropathology was normal in the rats, guinea pigs and dogs, however, adverse effects were noted in the livers of rabbits of both sexes. In the male rabbits this was characterized by central lobular granular degeneration and necrosis with some foamy vacuolation. In the female rabbits the changes noted were central lobular granular degeneration and necrosis with periportal cellular infiltration. All organ weights were normal except for the livers of the male and female rats which were increased significantly after repeated daily 7-hour exposures (Tables I, II, IV, V, VI, and VII). In the males this increase was still apparent eight weeks after exposure ceased, although the liver weights appeared to be decreasing and returning to normal.

The male rats exposed to 200 ppm of vinyl chloride for either four or two hours per day for six months had elevated average liver weights (Table I). However, the small size of the experimental groups made the finding statistically insignificant (P = 0.07 and 0.1). The groups exposed for either 1 or 0.5 hours per day were entirely normal.

TABLE II

Summary of Average Body and Organ Weights of Female Rats Receiving Repeated 7-Hour Exposures to Vinyl Chloride 5 Days per Week

Concentration in ppm	Months on Exposure	Ratio of Survival	Final Average Body Weight, g	Organ Weights, g/100 g Body Weight				
				Lung	Heart	Liver	Kidney	Spleen
Unexposed control	0	5/5	194	0.82	0.41	3.06	0.80	0.19
500	4.5	9/10	195	0.68	0.38	3.22[a]	0.81	0.20
Unexposed control	0	10/12	202	0.65	0.38	2.92	0.82	0.17
Air exposed control	6	9/12	223	0.66	0.39	2.99	0.81	0.18
200	6	10/12	208	0.63	0.38	3.39[b]	0.84	0.18
100	6	11/12	221	0.59	0.39	3.35[c]	0.79	0.20
Unexposed* control	0	8/12	223	0.61	0.37	2.67	0.82	0.18
Air exposed* control	6	9/12	240	0.58	0.37	2.97	0.83	0.18
200*	6	12/12	233	0.61	0.38	3.06	0.81	0.20
100*	6	12/12	235	0.63	0.40	3.17	0.83	0.21
Unexposed control	0	11/12	211	0.58	0.39	3.02	0.83	0.20
Air exposed control	6	12/12	202	0.59	0.38	2.93	0.84	0.20
50	6	9/12	206	0.61	0.37	3.02	0.84	0.20
Unexposed** control	0	11/12	195	0.66	0.40	2.88	0.91	0.22
Air exposed control**	6	9/12	221	0.63	0.40	3.01	0.87	0.19
50**	6	11/12	233	0.63	0.38	2.83	0.82[d]	0.20

* Pastured for 8 weeks after exposures ceased.
** Pastured for 6 weeks after exposures ceased.
(a) P = 0.17
(b) P = 0.03
(c) P = 0.01
(d) P = 0.05

Exposure to 100 ppm Vinyl Chloride

All species exposed to 100 ppm of vinyl chloride, seven hours per day, 138–144 times in 204 days, were judged normal on the basis of the following criteria: appearance, mortality, growth, hematological examination, SUN, SGOT, S-GPT, alkaline phosphatase determination, urinalysis and gross and microscopic examination of tissue. However, slight increases were found in the average weights of the livers of male and female rats (Tables I and II). Although not significant statistically, an increase was also seen in the average weight of the livers of the male rats exposed to 100 ppm for either four or two hours per day. The groups exposed for either 1.0 or 0.5 hour per day were entirely normal.

Exposures to 50 ppm Vinyl Chloride

The increase in weight of the rat livers, the only significant finding in animals exposed to 100 ppm, did not occur in rats exposed repeatedly to 50 ppm of vinyl chloride, 130 times in 189 days. All groups of animals were judged normal in all other respects. See Tables II, V, VI, VII, VIII and IX. A statistically significant decrease in kidney weight which was seen in the female rats (Table II) was considered to be an artifact since it was not seen at higher concentrations.

Discussion

Repeated exposure to vinyl chloride at concentrations considerably below the level that has been considered safe for human exposure has been shown to have an effect on the liver and kidney of laboratory animals. Histopathological changes and increased liver weights in male and female rats were noted after repeated exposure at 500 ppm. Repeated exposure at 200 ppm for six months resulted in an increase in the average weight of the livers of male and female rats and micropathological changes in the livers of the male and female rabbits. The only effect noted after repeated daily 7-hour exposures to 100 ppm for six months was a slight increase in the average weight of the rat livers. Repeated 7-hour exposures to 50 ppm for six months had no effect on any species studied. Hence, the highest concentration without detectable effect on any species was 50 ppm.

It is interesting to speculate on the apparent discrepancy between the effects observed at 100 ppm in this experiment and the lack of reported injury in humans using a threshold limit of 500 ppm. Several factors may be contributory. First, the effects noted in animals at 500 ppm were only slight to moderate; growth, mortality, and general appearance were unaffected. Hence, it is possible that if humans were exposed repeatedly at 500 ppm slight injury might occur but due to the lack of subjective symptoms the injury would escape detection. Secondly, the injury was apparently reversible. The liver weights of both male and female rats which had shown definite increases after exposures at 200 and 100 ppm were normal or approaching normal after 6–8 weeks of recovery (Tables I, II and VIII).

TABLE III

Summary of Average Biochemical Values Determined for Animals Receiving Repeated Exposures to Vinyl Chloride 5 Days per Week

Species and Dog No.	Sex	Concentration in ppm	Months on Exposure	Duration of Daily Exposure, hours	Number of Animals	Alkaline Phosphatase King-Armstrong Units	Blood Urea Nitrogen, mg/100 ml	SGPT	SGOT
								Sigma-Frankel Unit	
Dog #101	M	Unexposed control	0	0	1	12.2	24	18	43
#113		Air exposed control	6	7	1	4.1	19	19	17
#41		200	6	7	1	8.6	11	18	48
#98		100	6	7	1	4.5	16	21	19
Dog #106	F	Unexposed control	0	0	1	5.1	11	10	26
#107		Air exposed control	6	7	1	7.1	20	14	17
#103		200	6	7	1	7.9	14	16	26
#110		100	6	7	1	5.6	10	10	14
Rat	M	Unexposed control	0	0	5	32.9*	20.6*	30	
		500	4.5	7	4	18.9	13.8	35	
		200	6	7	5	17.7	16.2	36	
		200	6	4	4	18.4	16.2	32	
		200	6	1	3	20.2	17.7	42	
		100	6	7	4	19.4	15.0	27	
		100	6	4	3	14.7	16.3	36	
		100	6	1	3	19.0	15.3	30	
Rat	F	Unexposed control	0	0	4	12.1	20.5	38	
		500	6	7	3	16.1	22.3	26	
		200	6	7	5	13.6	22.2	21	
		100	6	7	6	9.5	22.8	23	
Rabbit	M	Control	6	0	5	4.0	25	36	
		200	6	7	3	5.3	21	23	
		100	6	7	2	5.9	26	26	
Rabbit	F	Control	6	0	6	4.9	33	38	
		200	6	7	2	5.6	27	35	
		100	6	7	3	4.0	26	35	

* Because of two unusually high individual values in this group these average values are elevated and do not correspond with the values obtained on similar control groups in our laboratory. Normal control values are in the same ranges as those of the experimental groups listed in this table.

TABLE IV

Summary of Average Hematological Values for Animals Receiving Repeated 7-Hour Exposures to Vinyl Chloride

Species or Dog #	Sex	Concentration in ppm	Months on Experiment	No. of Animals	Hemoglobin g/100 g	Hematocrit	WBC × 10^3	Neutrophils	Lymphocytes	Monocytes	Eosinophils
Rat	M	Air exposed control	6	4	14.5	51	15.8	26.5	71.2	1.5	0.8
Rat	M	200	6	5	14.4	50	16.7	19	77.8	0.2	3
Rat	F	Air exposed control	6	4	14.0	49.5	13.5	22.5	74.5	0.2	2.8
Rat	F	200	6	5	13.5	47.4	12.8	24.8	70.2	1.0	4
Dog #101	M	Unexposed control	0	1	—	—	—	—	—	—	—
Dog #101	M	Unexposed control	6	1	15	53	14.2	46	51	0	3
Dog #113	M	Air exposed control	0	1	14.5	50	13.5	61	23	5	11
Dog #113	M	Air exposed control	6	1	14.5	52	13.2	58	34	4	4
Dog #111	M	200	0	1	13	47	16.2	56	28	3	13
Dog #111	M	200	6	1	16.5	58	15.8	56	41	2	1
Dog #98	M	100	0	1	15.5	52	19.8	46	46	4	4
Dog #98	M	100	6	1	16	54	18.6	61	39	0	0
Dog #106	F	Unexposed control	0	1	14.5	51	21.8	42	37	3	18
Dog #106	F	Unexposed control	6	1	15.5	54	16.5	54	41	1	4
Dog #107	F	Air exposed control	0	1	15	53	14.4	55	33	4	8
Dog #107	F	Air exposed control	6	1	16	57	11.7	66	23	4	7
Dog #103	F	200	0	1	14	50	17.5	44	48	3	5
Dog #103	F	200	6	1	16	54	17.3	46	51	0	3
Dog #110	F	100	0	1	12.5	44	16.3	61	37	2	0
Dog #110	F	100	6	1	15.5	54	14.4	49	50	1	0

TABLE V

Summary of Terminal Average Body and Organ Weights of Guinea Pigs Receiving Repeated Daily 7-Hour Exposures to Vinyl Chloride 5 Days per Week for 6 Months

Sex	Concentration in ppm	Ratio of Survival	Final Average Body Weight, g	Organ Weights, g/100 g Body Weight					
				Lung	Heart	Liver	Kidney	Spleen	Testes
M	Unexposed control	8/10	927	0.64	0.28	3.32	0.70	0.16	0.48
M	Air exposed control	5/10	1030	0.52	0.28	3.36	0.61	0.10	0.48
M	200	7/10	1044	0.53	0.27	3.01	0.60	0.09	0.44
M	100	7/10	1089	0.52	0.25	2.79[a]	0.58	0.11	0.47
M	Unexposed control	8/12	918	0.60	0.29	3.24	0.68	0.12	0.52
M	Air exposed control	11/12	936	0.61	0.27	3.31	0.64	0.12	0.50
M	50	10/12	1001	0.63	0.26	3.14	0.61	0.12	0.48
F	Unexposed control	6/8	899	0.62	0.27	3.20	0.63	0.12	
F	Air exposed control	7/8	867	0.66	0.25	3.28	0.67	0.11	
F	200	7/8	897	0.74[b]	0.27	3.60[c]	0.66	0.13	
F	100	7/8	949	0.58	0.26	3.50	0.64	0.12	
F	Unexposed control	9/12	728	0.78	0.34	3.41	0.69	0.15	
F	Air exposed control	8/12	884	0.65	0.26	3.84	0.65	0.14	
F	50	11/12	906	0.69	0.28	3.44	0.64	0.14	

(a) P = 0.05
(b) P = 0.24
(c) P = 0.23

TABLE VI

Summary of Terminal Average Body and Organ Weights of Rabbits Receiving Repeated Daily 7-Hour Exposures to Vinyl Chloride 5 Days per Week for 6 Months

Sex	Concentration in ppm	Ratio of Survival	Final Average Body Weight, kg	Organ Weights, g/100 g Body Weight					
				Lung	Heart	Liver	Kidney	Spleen	Testes
M	Unexposed	3/3	3.61	0.39	0.21	2.27	0.43	0.03	0.16
M	Air exposed control	2/3	3.90	0.31	0.18	2.41	0.46	0.02	0.16
M	200	3/3	3.48	0.32	0.19	2.34	0.54	0.02	0.15
M	100	3/3	3.65	0.33	0.18	2.64	0.49	0.02	0.15
M	Unexposed control	2/3	3.80	0.32	0.17	2.33	0.45	0.02	0.15
M	Air exposed control	1/3	3.87	0.37	0.18	3.18	0.53	0.03	0.14
M	50	3/3	3.70	0.36	0.20	2.46	0.47	0.03	0.17
F	Unexposed	3/3	4.13	0.31	0.17	2.22	0.40	0.03	
F	Air exposed control	3/3	3.91	0.30	0.18	2.18	0.41	0.04	
F	200	2/3	4.10	0.32	0.16	2.26	0.42	0.05	
F	100	3/3	4.12	0.29	0.18	1.87	0.38	0.05	
F	Unexposed control	3/3	4.31	0.30	0.17	1.94	0.46	0.04	
F	Air exposed control	2/3	3.95	0.30	0.17	1.88	0.39	0.04	
F	50	3/3	4.31	0.32	0.17	2.49	0.38	0.04	

TABLE VII

Summary of Final Body and Organ Weights of Dogs Receiving Repeated Daily 7-Hour Exposures to Vinyl Chloride 5 Days per Week for 6 Months

Sex	Dog. No.	Concentration in ppm	Ratio of Survival	Final Body Weight, kg	Organ Weights, g/100 g Body Weight					
					Lung	Heart	Liver	Kidney	Spleen	Testes
M	101	Unexposed control	1/1	13.0	0.66	0.62	2.46	0.38	0.32	0.15
M	113	Air exposed control	1/1	8.5	0.68	0.77	2.63	0.47	0.19	0.14
M	111	200	1/1	10.2	1.03	0.96	2.50	0.52	0.25	0.13
M	98	100	1/1	12.0	0.86	0.80	2.50	0.42	0.26	0.15
M	152	Unexposed control	1/1	13.3	0.80	0.75	2.69	0.53	0.23	0.11
M	156	Air exposed control	1/1	10.6	0.77	0.87	3.05	0.45	0.36	0.14
M	162	50	1/1	9.6	0.89	0.78	2.40	0.45	0.23	0.12
F	106	Unexposed control	1/1	9.6	0.71	0.68	2.67	0.43	0.21	
F	107	Air exposed control	1/1	8.7	0.77	0.80	3.15	0.43	0.33	
F	103	200	1/1	10.5	0.78	0.71	1.88	0.45	0.28	
F	110	100	1/1	11.9	0.99	0.78	2.14	0.43	0.31	
F	151	Unexposed control	1/1	8.6	0.99	0.82	4.10	0.45	0.43	
F	155	Air exposed control	1/1	11.3	0.70	0.84	3.31	0.40	0.25	
F	161	50	1/1	7.4	0.87	0.76	2.48	0.47	0.33	

TABLE VIII

Summary of Terminal Average Body and Organ Weights of Male Rats Receiving Repeated Exposures to Vinyl Chloride 5 Days per Week

Concentration in ppm	Months on Exposure	Duration of Daily Exposure, hours	Ratio of Survival	Final Average Body Weight, g	Organ Weights, g/100g Body Weight					
					Lung	Heart	Liver	Kidney	Spleen	Testes
Unexposed control	0	0	8/8	319	0.50	0.33	2.67	0.75	0.18	0.98
Air exposed control	6	7	12/12	347	0.51	0.32	2.41	0.70	0.16	0.81
50	6	7	12/12	339	0.50	0.31	2.49	0.68	0.17	0.87
50	6	4	8/10	348	0.51	0.33	2.59	0.69	0.16	0.81
50	6	2	6/10	322	0.49	0.32	2.57	0.70	0.16	0.80
50	6	1	9/10	348	0.47	0.32	2.51	0.73	0.17	0.84
Unexposed* control	0	0	8/8	336	0.53	0.32	2.37	0.72	0.16	0.83
Air exposed* control	6	7	12/12	370	0.53	0.30	2.42	0.64	0.14	0.75
50*	6	7	12/12	360	0.49	0.33	2.51	0.68	0.15	0.82

* Pastured for 6 weeks after exposures ceased.

Thirdly, it is doubtful whether it would be possible for humans to be exposed continuously at 500 ppm in production plants since this high a general concentration would indicate severe leaks in the equipment and extremely high concentrations

TABLE IX

Summary of Average Hematological Values for Dogs Receiving Repeated 7-Hour Exposures to Vinyl Chloride

Dog #	Sex	Concentration in ppm	Months on Experiment	No. of Animals	Hemoglobin g/100 g	Hematocrit	WBX × 10^3	Neutrophils	Lymphocytes	Monocytes	Eosinophils
Dog #152	M	Unexposed control	0	1	11	43	12.9	54	41	1	4
Dog #152	M	Unexposed control	3	1	15	52	19.4	42	50	4	4
Dog #152	M	Unexposed control	6	1	15.5	54	15.4	52	40	5	3
Dog #156	M	Air exposed control	0	1	—	—	—	—	—	—	—
Dog #156	M	Air exposed control	3	1	14.5	50	13.4	45	50	2	3
Dog #156	M	Air exposed control	6	1	14	50	11.1	55	28	5	12
Dog #162	M	50	0	1	10.5	39	13.6	48	48	2	2
Dog #162	M	50	3	1	14.5	54	12.7	48	48	3	1
Dog #162	M	50	6	1	15.5	53	11.2	43	50	4	3
Dog #151	F	Unexposed control	0	1	11	48	13.3	59	30	3	9
Dog #151	F	Unexposed control	3	1	14.5	52	23.6	67	25	0	8
Dog #151	F	Unexposed control	6	1	15.5	58	15.5	46	42	3	9
Dog #155	F	Air exposed control	0	1	13	46	14	61	37	0	2
Dog #155	F	Air exposed control	3	1	16	59	18.2	60	33	5	2
Dog #155	F	Air exposed control	6	1	15.5	56	17.0	53	31	5	11
Dog #161	F	50	0	1	10.5	35	15.3	55	40	5	0
Dog #161	F	50	3	1	15.5	58	13.4	56	42	2	0
Dog #161	F	50	6	1	15.5	56	12.3	43	43	3	11

adjacent to the leaks. The flammability of vinyl chloride precludes such severe leaks if this hazard of vinyl chloride is to be controlled.

Industrial Hygiene Standard

The data presented indicate that little likelihood of injury would be expected if repeated daily 7- to 8-hour exposures are limited to 100 ppm or less.

Although the level of 100 ppm may not appear to offer any margin of safety since rats exposed repeatedly to this level were very slightly affected, the vast amount of human experience that is available while operating under an MAC of 500 ppm indicates that injury is not likely. Likewise the effects of even rather severe overexposure are not serious, hence this level seems reasonable.

A time-weighted average for all exposure should probably not exceed 50 ppm.

Summary

Vinyl chloride (CH_2=CHCl) is a monomer used in very large quantities in the production of plastics. Repeated exposures of laboratory animals to several concentrations of vinyl chloride in air were conducted to determine the chronic toxicity of this material towards animals in order to assess the hazard to humans. Vinyl chloride was found to have a slight capacity to cause liver and kidney injury on repeated exposures. Male and female rats showed micropathological changes after repeated daily 7-hour exposures at 500 ppm for 4.5 months. Repeated 7-hour exposures at 200 ppm for six months resulted in micropathological changes in the livers of rabbits and statistically significant increases in the average weight of the livers of male and female rats but no detectable changes in dogs and guinea pigs. Repeated 7-hour exposures at 100 ppm resulted in slight increases in the average weight of rat livers, the other species were not affected. All species studied tolerated repeated daily 7-hour exposures to 50 ppm for six months with no detectable injury.

Repeated daily 1-hour exposures at 200 and 100 ppm of vinyl chloride were without effect, longer exposures caused a slight increase in liver weight.

The standard for evaluating regular daily 7- to 8-hour exposures may be defined as the concentration below which practically all analytical results must fall. The value of 100 ppm is suggested as this standard for vinyl chloride, with a time-weighted average for all exposures not to exceed 50 ppm.

References

1. Manufacturing Chemists Assoc. Chemical Safety Data Sheet SD-56 (1954).
2. VON OETTINGEN, W. F.: *The Halogenated Hydrocarbons, Toxicity and Potential Dangers.* (U. S. Public Health Service, Publication No. 414.) Government Printing Office, Washington, D. C. (1955).
3. MASTROMATTEO, E., A. M. FISHER, H. CHRISTIE, AND D. DANZIGER: Acute Inhalation Toxicity of Vinyl Chloride to Laboratory Animals. *Am. Ind. Hyg. Assoc. J. 21:* 394 (1960).
4. SCHAUMANN, O., cited by K. B. LEHMAN AND F. FLURY,

Toxicol. u. Hyg. der technischen Losungsmittel, J. Springer, Berlin, 1938 p. 130. (From the translation, *Toxicology and Hygiene of Industrial Solvents* by E. King and H. F. Smyth, Jr., 1941).
5. A.C.G.I.H. Threshold Limit Values for 1960. *AMA Arch. of Envir. Health 1:* 62 (1960).
6. SMYTH, H. F., JR.: Improved Communication—Hygiene Standards for Daily Inhalation. *Am. Ind. Hyg. Assoc. J. 17:* 129 (1956).
7. Cherry Hill Farms, Camden, New Jersey.
8. Ralston Purina Company, St. Louis, Missouri.
9. Harris Milling Company, Mount Pleasant, Michigan.
10. SPENCER, H. C., V. K. ROWE, E. M. ADAMS, D. D. MCCOLLISTER, AND D. D. IRISH: Vapor Toxicity of Ethylene Dichloride as Determined by Experiments on Laboratory Animals. *AMA Arch. Ind. Hyg. and Occup. Med. 4:* 482 (1951).
11. TORKELSON, T. R., M. A. WOLF, F. OYEN, AND V. K. ROWE: Vapor Toxicity of Allyl Chloride as Determined on Laboratory Animals. *Am. Ind. Hyg. Assoc. J. 20:* 217 (1959).
12. Dual Syringe Feeder Pumps, Modern Metalcraft, Midland, Michigan.

Industrial Hygiene Certification

THE AMERICAN BOARD OF INDUSTRIAL HYGIENE invites inquiries from those who are interested in applying for voluntary certification in the profession of industrial hygiene. Certificates will be issued on the basis of an examination to those who have eight years of practice, following a suitable baccalaureate degree. No examination will be required of those who have fifteen years of practice with recognized contributions to the field, following acceptable education. Certain specialists within the field will be certified when one-fourth of their time has consistently been devoted to application of their specialty to industrial hygiene. A brochure describing the certification program, and giving more details of eligibility will be sent to those who direct inquiries to Henry F. Smyth, Jr., Secretary-Treasurer, American Board of Industrial Hygiene, 4400 Fifth Avenue, Pittsburgh 13, Pennsylvania.

The Board was chartered as a non-profit corporation under the laws of the Commonwealth of Pennsylvania in September 1960. The incorporators were selected by the American Conference of Governmental Industrial Hygienists and the American Industrial Hygiene Association from among their respective memberships. They are John C. Soet, Chairman; Lester V. Cralley, Ph.D., Vice-Chairman; Henry F. Smyth, Jr., Ph.D., Secretary-Treasurer; and Edgar C. Barnes, William R. Bradley, Allan L. Coleman, Hervey B. Elkins, Ph.D., Louis F. Garber, Thomas F. Mancuso, M.D., Kenneth M. Morse, James H. Sterner, M.D., and Charles D. Yaffe.

Industrial Hygiene Engineering and Chemistry

THE DIVISION OF OCCUPATIONAL HEALTH, Public Health Service, will conduct two simultaneous courses January 8–19, 1962, at the Occupational Health Research and Training Facility, Cincinnati, Ohio. "Industrial Hygiene Engineering" is designed for industrial hygienists and engineers in the field of occupational health who have a degree in engineering or in the physical sciences. "Industrial Hygiene Chemistry" is designed for chemists in this field who have a degree in chemistry or chemical engineering, or in the physical sciences with a minor in chemistry. During the first week, trainees for both courses meet together for instruction in industrial hygiene and medicine, toxicology, and principles pertaining to evaluation of the environment. For the hygienists, the second week's work covers temperature and humidity measurements, illumination, noise measurement and control, and industrial ventilation; for the chemists, laboratory analyses for lead, free silica, and solvents, and spectroscopy, polarography, x-ray diffraction, electron microscopy, and gas chromatography. Much time in both courses is spent in the laboratory.

It should be noted that applications for the course or requests for information should be addressed to the Chief, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio, or to a DHEW Regional Office Director.

The Measurement of Phenol in Urine As An Index of Benzene Exposure

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The measurement of phenol as a metabolic product of benzene was investigated in relation to its usefulness in evaluating exposures to benzene. Phenol was distilled from the urine and determined colorimetrically by a p-nitroaniline procedure. The average phenol content of normal urine is 30 mg/liter as determined by this method. Concentrations of phenol found in the urine of workers exposed to benzene and benzene-containing solvents were correlated with benzene concentrations in the air of the workrooms. A urinary phenol value of about 200 mg/liter was found for workers exposed to an average of 25 ppm of benzene in air.

IN ESTIMATING exposure to industrial poisons, air samples are commonly used for determining general or local concentrations in the workroom. Since operations may be intermittent, and personnel may rotate on various jobs, it is sometimes difficult to evaluate the exposure of an individual or group of workers by means of air tests or clinical examinations. For certain industrial processes, it is possible to resort to measurement of excreted metabolites of the material to which the worker is exposed. In this country it has been the practice to estimate exposure to benzene by means of the urine sulfate ratio test originally proposed by Yant *et al.*[1] It is the purpose of this paper to present an alternate test which has been found preferable from the point of view of sensitivity and specificity.

Background

The commonly used urine sulfate ratio test is based on the premise that benzene is partially metabolized to organic derivatives conjugated with sulfate radicals. As these so-called "ethereal sulfates" increase due to exposure to benzene, there is a corresponding decrease in the ratio of inorganic to total sulfates. According to Elkins[2] the following interpretation may be applied:

Ratio of Inorganic to Total Sulfate	Extent of Benzene Exposure
Above 80%	None
70–80%	Mild
30–70%	Unsafe
Below 30%	Dangerous

In 1916 Brewer and Weiskotten[3] demonstrated that benzene was partially excreted as phenol conjugates. According to Porteous and Williams[4] the probable sequence of the metabolism of benzene is as follows:

Benzene → Phenol → Catechol → Hydroxyquinol

Studies by Parke and Williams[5] using tagged benzene indicated that about 23% of an oral dose of benzene in rabbits is excreted as conjugated phenol, and that other phenols excreted are quinol (4.8%), catechol (2.2%) and hydroxyquinol (0.3%). The same authors later reported[6] that 6 to 8% of an oral dose is excreted within 48 hours as phenylglucuronide and 11 to 14% as phenylsulfuric acid. Deichmann and Thomas[7] attempted to apply the determination of glucuronic acid in urine as a measure of the absorption of various organic compounds, but this test was not specific or particularly sensitive to benzene.

Recently Teisinger and Fiserova-Bergerova[8] proposed the determination of phenols in urine as a sensitive test for human exposure to benzene. By this method the phenol present as both glucuronate and sulfate is determined. The authors state that according to their experience an average of 30% of absorbed benzene is excreted in the form of phenol. They believe that an individual value of less than 40 mg of phenol per 24 hours indicates exposure to less than 25 parts per million of benzene, and that an average collective value of 100 mg per 24 hours indicates

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that air concentrations are close to 25 ppm. Up to a phenol level of 288 mg/liter they found a linear relationship with organic sulfates, but above this level phenol increases while the organic sulfate remains constant. Their findings are based on data from humans exposed in chamber studies and in the field.

Normal Values

The apparent phenol content of normal urine depends to some extent on the method of preparation and analysis of samples. In the investigation mentioned above, Teisinger and Fiserova-Bergerova[8] found an average of 8.2 mg of total phenol per day using the method proposed by Gibbs.[9] By the same method Porteus and Williams[4] in this country reported 5 to 10 mg per liter. Deichmann and Schafer[10] using diazotized p-nitroaniline as proposed by Theis and Benedict[11] found values for total phenol ranging from 11 to 42 mg per day, with an average of 25. A modification of this method is the one adopted in our laboratory, where a range of 15 to 50 milligrams per liter was found, with an average of 30. Our values have been adjusted to a mean specific gravity of 1.024.

Subsequent measurements on unexposed individuals showed occasional higher values. One person who had been taking analgesics regularly had consistent phenol levels of 100 to 200 mg/liter. Ingestion of phenacetin, caffeine, and saccharin by other subjects failed to give comparable results. While levels as high as 100 mg/liter appeared in some cases, there was no significant change in others.

Analytical Method

Several methods of sample preparation and analysis were investigated before the final one was adopted. Following the methods referred to by Deichmann and Schafer[10] attempts were made to separate phenol by solvent extraction as well as by precipitation of interferences, but it became obvious that neither method was satisfactory without further separation. It was found that phenol was recovered quantitatively by steam distillation and that a minimum of interferences was carried over by this method. The two most promising analytical methods appeared to be those of Gibbs[9] using 2,6-dichloroquinonechloroimide and Theis and Benedict[11] using diazotized p-nitroaniline. Although the method of Gibbs gives slightly lower results and appears to be somewhat more specific for phenol, it proved to be critical in regard to pH adjustment as well as time of color development. It was found that the method of Theis and Benedict as modified is much better suited to routine determination of phenol in a large number of samples, since it does not require a careful pH adjustment, color may be compared almost immediately, and reproducibility is excellent even in the hands of inexperienced personnel. The method which follows is that used in our laboratory to obtain the data presented in the latter part of this paper.

The sample may consist of a single voiding collected at the end of the working day. Specific gravity must be obtained in order to adjust final results to a mean of 1.024. If impractical to analyze samples immediately, they may be preserved by refrigeration over long periods of time. For analysis a 10 ml aliquot is pipetted directly into the flask of an all-glass apparatus equipped for steam distillation. Four ml of 1:1 H_2SO_4 is added, and the sides of the flask are washed down with approximately 5 ml of distilled water. The apparatus is connected and steam generation begun. When steam starts to bubble through the sample, a low flame may be placed under the sample flask to maintain sufficient temperature for distillation without appreciable change in volume. Care must be taken that the sample does not become overheated to the point of dryness. The distillate is collected in a graduated cylinder to a total volume of 100 ml, then transferred to a bottle or flask for mixing and storage if necessary. A 10 ml aliquot is transferred to a 25 ml glass stoppered graduate for phenol determination. One ml of 50% sodium acetate is added followed by one ml of p-nitroaniline reagent. After exactly one minute, 2 ml of 20% sodium carbonate is added, and the total volume made up to 20 ml. After three minutes the color is compared with a blank at 525 mμ or with a suitable filter. When a 10 ml aliquot is used, the result in micrograms is equivalent to milligrams per liter of urine. Standards should be made up using 0–100 μg of phenol. Sensitivity is about 4 μg or 4 milligrams of phenol per liter of urine when a 10 ml aliquot of distillate is used.

Reagents

Sodium Acetate: 50% solution.

p-Nitroanaline Reagent: Weigh out 0.75 gram p-nitroaniline, add 5–10 ml distilled water and 20 ml concentrated HCl. Dilute to 250 ml and filter, if necessary. Prepare diazotized reagent fresh daily by adding 1.5 ml of 5% $NaNO_2$ to 25 ml of this solution.

Sodium Carbonate: 20% solution.

Phenol Standard: Weigh out exactly 0.500 gram of purified phenol, add about 10 ml distilled water and 4 ml concentrated HCl. Dilute

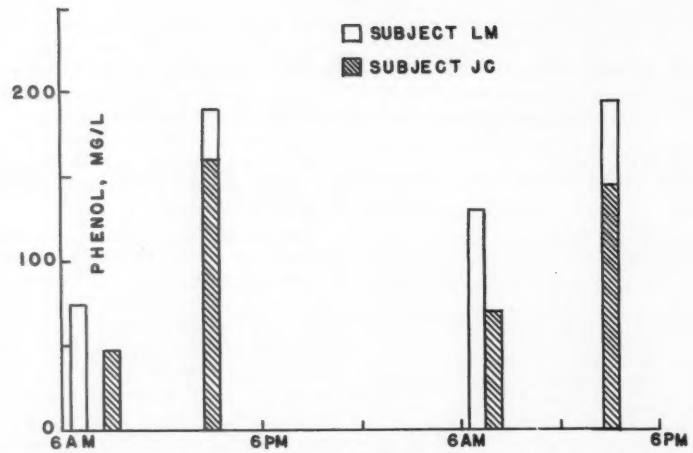

FIGURE 1. Diurnal variation of phenol excretion by two workers exposed to an average daily concentration of less than 25 ppm of benzene.

TABLE I

Comparison of Urinary Phenol Values with Sulfate Ratios Obtained on the Same Samples

No. of Workers	Average Phenol (mg/liter)	Average SO_4 Ratio
Normal values	30	Above 80%
14	35	89%
7	91	88%
5	202	73%

to 500 ml for stock solution. For working standard dilute one ml to 100, and use 1 to 10 ml (10 to 100 μg) for curve.

Interferences

Although cresol, resorcinol, and higher phenol homologues may produce color with the reagent, the net interference should be slight since they are either removed by distillation or are not present in normal urine in sufficient quantity to produce a significant effect. However, 2,5-dichlorophenol, which has been found in the urine of paradichlorobenzene workers, also reacts with p-nitroaniline. Its presence may be confirmed by the use of Gibbs' reagent with which it produces a color with maximum absorbance at 675 mμ in contrast to the maximum of 605 mμ given by phenol. About 300 μg of aspirin in solution gave no color, and there was no increase in phenol in the urine two hours after ingestion of two 5-grain tablets. Benzene and its homologues give no reaction, and there appears to be no increase in urinary phenol after exposure to low concentrations of toluene or xylene.

Human Exposure Data

Various samples from persons exposed both in a chamber and in the field have been analyzed. The exposures in the field were to benzene alone as well as to petroleum naphthas having a low benzene content.

Preliminary studies were conducted on workers who were regularly exposed to low concentrations of benzene. In the plant selected, normal air concentrations were below 25 parts per million as determined routinely by direct-reading tubes. Results from two workers, as shown in Figure 1 demonstrate that the urinary phenol content shows a definite increase following exposure to benzene. Values decrease on the following morning, although they do not necessarily return to normal.

As an additional study in the same plant, phenol concentrations in the urine were compared with sulfate ratios on a number of workers. Included were samples from benzene-exposed workers both before and at the end of the work day, as well as four samples from a clerical worker in the plant. The results as shown in Table I illustrate the greater sensitivity of the phenol test as compared to the urine sulfate ratio. As an example, a sulfate ratio of 88% would be considered to be in the normal range of unexposed persons, whereas the corresponding phenol concentration of 91 mg/liter indicates definite exposure to concentrations of benzene

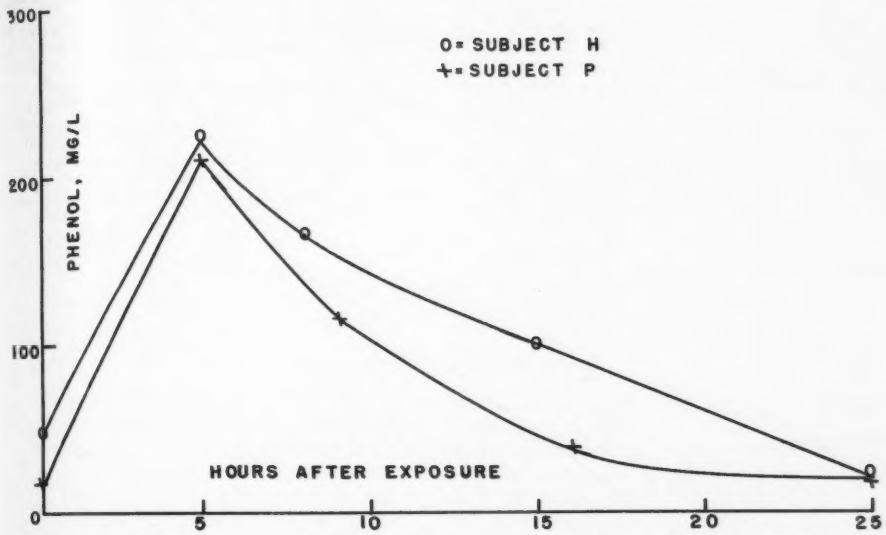

FIGURE 2. Phenol excretion of two subjects exposed in a chamber to 200 ppm of benzene for 30 minutes. Subject H was exercising moderately, while subject P was sedentary.

below the current Threshold Limit Value (TLV) of 25 ppm.

Through the co-operation of the Harvard School of Public Health, samples were obtained from two previously unexposed persons who were subjected to a single known concentration of 200 ppm of benzene for thirty minutes. During the exposure subject H was exercising moderately, while subject P was sedentary. Results are presented graphically in Figure 2 and show the rapid initial rise in phenol content followed by return to normal within 24 hours. Total post-exposure phenol excretion by subject H was 69.9 milligrams and by subject P was 57.7 milligrams.

In order to obtain a more reliable correlation between air and urine values, air samples were taken on silica gel, and benzene determined by solvent extraction and comparison of the ultraviolet absorption with standards.[12] Urine samples from workers were obtained on the same day near the end of the work period and analyzed by the method previously described. Thus far our field investigations have been concerned primarily with the rubber coating industry where the naphtha used may have a natural benzene content of 1.5 to 9.3% by weight.[12]

Results obtained in a single plant are shown in Table II. As might be expected with a small sample, some results appear to be inconsistent. In the data used, however, it was assumed that the air samples taken were representative of the exposure over the entire day. Frequently this is not the case, as operations may be variable or intermittent over the work period.

TABLE II

Typical Benzene Air Values and Urinary Pheno Concentrations Obtained in a Survey of a Single Plant

Benzene (ppm)	No. of Workers	Phenol (mg/liter)
5	1	68
7	1	75
11	1	114
12	2	109
15	3	169
24	2	163
27	1	225
57	2	345
68	1	570

Data based on 43 air samples and 69 urine samples are plotted in Figure 3 to show correlation between urinary phenol and benzene air values. On the basis of these findings it appears that exposure to benzene in excess of the present TLV of 25 ppm will be reflected by a urinary phenol concentration of more than 200 mg/liter.

When applying the phenol test, the following factors should be considered:

1. Since phenol is apparently excreted rapidly,

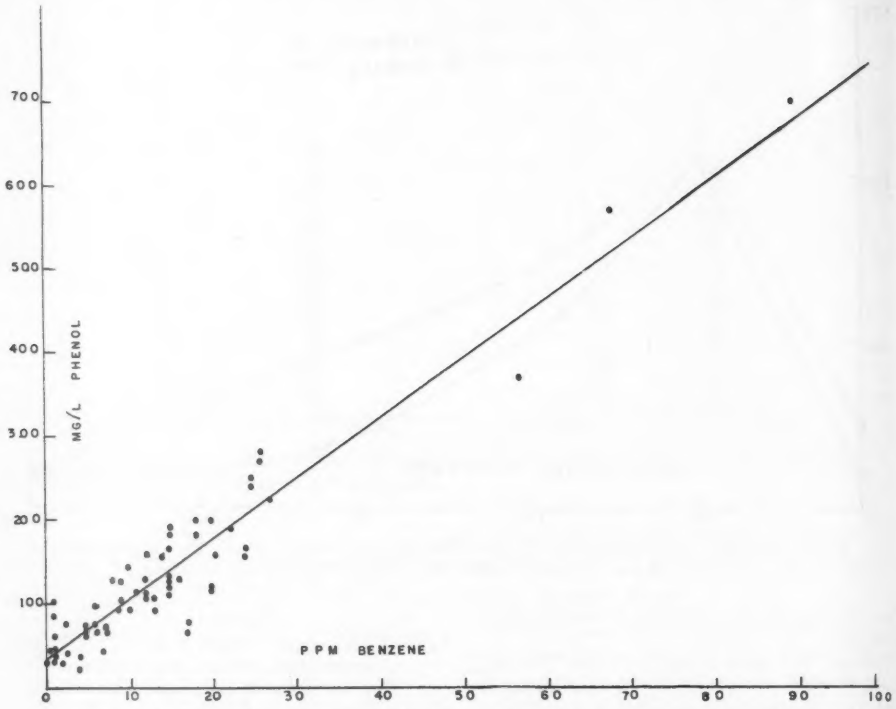

FIGURE 3. Comparison of urinary phenol excretion with benzene air concentrations.

results are significant only when applied to urine samples obtained at or near the end of the working period.

2. It is advisable to adjust all phenol values to a definite specific gravity for good correlation. In this laboratory a mean value of 1.024 is used.
3. The data presented are based on exposures to reasonably constant concentrations of benzene. Application of results to single acute exposures has not been thoroughly studied.
4. The phenol test has been found to give a more reliable picture of over-all benzene exposure than data obtained from air tests, however, it should not be used as an exclusive measure of exposure.

Summary and Conclusions

The application of a test for phenol in urine as an index of benzene exposure is discussed. It has greater sensitivity to low benzene concentrations than the previously used sulfate ratio, and has particular application where exposure is to low benzene concentrations or where interpretation of air sample data is difficult or unreliable. Data are given to illustrate the correlation between urinary phenol and benzene air concentrations obtained in field studies. From these studies it is concluded that a urinary phenol concentration of 200 milligrams per liter is indicative of exposure to approximately 25 ppm of benzene in air.

References

1. YANT, W. P., H. H. SCHRENK, R. R. SAYERS, A. A. HORVATH, AND W. H. REINHART: Urine Sulfate Determinations as a Measure of Benzene Exposure. *J. Ind. Hyg. & Toxicol. 18:* 69 (1936).
2. ELKINS, H. B.: *The Chemistry of Industrial Toxicology.* 2nd Ed., John Wiley & Sons, New York (1959).
3. BREWER, R. H., AND H. G. WEISKOTTEN: The Action of Benzol: III. The Urinary Phenols. *J. Med. Research. 35:* 71 (1916).
4. PORTEOUS, J. W., AND R. T. WILLIAMS: Studies in Detoxication, The Metabolism of Benzene I. *Biochem. J. 44:* 46 (1949).
5. PARKE, D. V., AND R. T. WILLIAMS: The Metabolism of Benzene Containing C^{14} Benzene. *Biochem. J. 54:* 231 (1953).

6. PARKE, D. V., AND R. T. WILLIAMS: Studies in Detoxication, 54, The Metabolism of Benzene. *Biochem. J. 55:* 337 (1953).
7. DEICHMANN, W., AND G. THOMAS: Glucuronic Acid in the Urine as a Measure of the Absorption of Certain Organic Compounds. *J. Ind. Hyg. & Toxicol. 25:* 286 (1943).
8. TEISINGER, J., AND V. FISEROVA-BERGEROVA: Valeur Comparée de la Détermination des Sulfates et du Phénol Contenus dans l'Urine pour l'Évaluation de la Concentration du Benzene dans l'Air. *Arch. Malad. Prof. 16:* 221 (1958).
9. SNELL, F. D., AND C. T. SNELL: *Colorimetric Methods of Analysis.* 3rd Ed., vol. III. D. van Nostrand, New York (1953).
10. DEICHMANN, W., AND L. J. SCHAFER: Phenol Studies. *Am. J. Clin. Path. 12:* 129 (1942).
11. THEIS, R. C., AND S. R. BENEDICT: The Determination of Phenol in the Blood. *J. Biol. Chem. 61:* 67 (1924).
12. PAGNOTTO, L. D., H. B. ELKINS, H. G. BRUGSCH, AND J. E. WALKLEY: Industrial Benzene Exposure from Petroleum Naphtha. *Amer. Ind. Hyg. Assoc. J. 22* (Dec. 1961) (in press).

Radioactive Pollutants in Air

THE PUBLIC HEALTH SERVICE, through its Division of Air Pollution, will conduct a one-week training course, "Radioactive Pollutants in Air," January 29–February 2, 1962, at Cincinnati, Ohio, for air pollution control officials, engineers, and other professional persons concerned with radioactive contamination of the air environment. The course provides instruction in air monitoring techniques including meteorological aspects, in sampling and analysis, and in the interpretation of data. One-third of the time is devoted to problem sessions and laboratory practice. Prior completion of the "Basic Radiological Health" course (given in Cincinnati, January 15–26, 1962), or equivalent training, is recommended. This course is followed by the related courses, "Radioactive Pollutants in Water" (February 5–9, 1962), and "Radionuclides in Water" (February 12–16, 1962).

Full descriptions of the courses are given in the *Training Program Bulletin* which is available on request. Address applications for the course or requests for information to the Chief, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio, or to a PHS Regional Office.

Correspondence Courses in Occupational Health

THE PROGRAM OF CONTINUATION EDUCATION of the Columbia University School of Public Health and Administrative Medicine, as an extension of its activities in postgraduate education, has prepared two additional home-study courses in the field of occupational health:

1. Industrial Applications of Ionizing Radiation
2. Industrial Hygiene

In each of the courses a text is provided and review questions have been prepared for each section of the texts. Students are invited to submit their answers to the review questions for correction.

Home-study courses in Biostatistics and Toxicology, formerly distributed through the American Academy of Occupational Medicine, are now available from the Program of Continuation Education. Inquiries regarding these correspondence courses should be addressed to:

The Program of Continuation Education-Occupational Medicine
Columbia University School of Public Health and Administrative Medicine
600 West 168th Street, New York 32, New York.

Spectrographic Determination of Lead in Whole Urine

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A method is presented for the determination of lead in urine without requiring the ashing of the urine. An internal standard, indium, is used in preference to bismuth. The method was developed for use in analytical laboratories which require a high degree of versatility. A nitrogen atmosphere is introduced around the sample electrode to reduce the wandering of the arc and to lower the spectral background.

ntroduction

LEAD-IN-URINE determinations have been made spectrographically for many years. Several methods have been described in the literature.[1, 2, 3, 4] Each method reviewed requires a complete ashing of the urine prior to analysis, although direct urine analysis without the ashing step can save considerable time. The method described accomplishes this objective. Other advantages include the reduction of the probability for contamination during analysis and also versatility with respect to numbers of samples for efficient utilization of equipment and personnel time.

Our laboratory, similar to other industrial hygiene laboratories, must be adapted to versatility as well as change in pace, from industrial study programs where hundreds of specimens are collected to the single analysis required by a physician who needs the results immediately to aid in diagnosis of critical cases. It is for this type of use that this method was developed. Previously, reported methods utilizing the internal standard technique recommended bismuth for this purpose. Since bismuth is used in medical therapy and is available to persons without prescriptions we felt that it would be advisable to seek another internal standard. We found indium meets the requirements and is used in the method described below.

Reagents and Standard Solutions

(All glassware is cleaned in concentrated HNO_3 and thoroughly rinsed with lead-free water after which it is dried in an oven at 105°C.)

1. Lead-free water.
2. Concentrated HNO_3, lead-free.
3. Standard solutions are prepared as follows: 1.598 g $Pb(NO_3)_2$ is weighed and made up to 1,000 ml in 10% HNO_3 giving a standard stock solution of one mg lead per ml. Aliquots are taken from this stock solution and made up to volume in 25 ml volumetric flask to give lead standards varying in concentrations from 0.2 micrograms Pb/0.5 ml to 5 micrograms Pb/0.5 ml in 10% HNO_3.
4. Spec-pure indium oxide (In_2O_3) used for internal standard:
   (a) Indium stock solution: 0.6045 g spectroscopically pure indium oxide (In_2O_3) is weighed into a 100-ml beaker, 10 ml concentrated HNO_3 added, heated and taken to dryness. (This step of converting the indium oxide to indium nitrate could be eliminated if spec-pure indium nitrate were used.) The indium nitrate in the 100-ml beaker is taken into solution with 10% HNO_3, transferred to a 1,000 ml volumetric, and made up to volume with 10% HNO_3. The solution contains 500 micrograms of In per ml.
   (b) Indium internal standard working solution: Transfer 12 ml of indium stock solution into a 100-ml volumetric flask and dilute to volume with distilled water. This solution contains 30 micrograms In per 0.5 ml.
5. Lithium chloride-graphite buffer mixture:[4] Spectroscopically pure graphite and C.P. lithium chloride are weighed out in a ratio of one part lithium chloride to 2.5 parts graphite, ground thoroughly in a mortar and stored over concentrated sulfuric acid in a desiccator.
6. Waterproofing solution: 2% solution of Dow Corning DC-702 fluid and C.P. acetone.

Equipment, Materials and Conditions

1. Bausch and Lomb Large Littrow, Region 5.
2. Optical conditions: Spectrograph slit width,

non-adjustable 10 microns; an image of the electrode is focused on the objective lens instead of the ordinary focusing on the slit. These optical conditions utilize the full speed of the instrument. The 10-micron slit, instead of the customary 20-micron slit, aids in reducing the spectral background.

3. Densitometer: Non-recording, National Spectrograph "Spec Reader".
4. Electrodes: (a) Lower electrode (anode); United Carbon Products Company, Ultra-Purity Preformed, Catalog No. 100-L, ¼-inch diameter; crater is 3/16-inch diameter and 5/32-inch deep.

   (b) Upper electrode (cathode) is 3/16-inch diameter, sharpened to a point in an ordinary de-leaded pencil sharpener. This also is a United Carbon Products electrode, Catalog No. ST-45.
5. Photographic: Eastman Kodak Spectrum Analysis No. 1 plate, developed 3.5 minutes in Eastman D-19 Developer at 68°F and fixed eight minutes in Eastman Koda-Fixer (National Spectrographic Developing Machine). Emulsion is calibrated by use of the two-step filter in front of the slit. The density of the filter section is given by Bausch and Lomb Company, makers of the filter.
6. Exposure conditions: 220 volts DC arc, operating at 7.5 amperes with a constant gap of 5 mm maintained between the anode and cathode. Exposure time is 24 seconds. Be certain that the anode is the lower electrode.
7. Nitrogen: Airco dry nitrogen, flow rate regulated by F. W. Dwyer Manufacturing Company flow meter, maximum flow rate six liters per minute; regulator 3,000 pounds.
8. Sample electrode holder construction[7] is shown is Figure 1. The nitrogen flow around the electrode is between three and four liters per minute.

Preparation of Electrodes

Preparation of the electrode for both standard curve and sample analysis is as follows: A ¼-inch diameter electrode is waterproofed by immersion in Dow Corning silicone solution (2% in acetone) and air dried for at least thirty minutes. A 5-mg charge of lithium chloride-graphite buffer is placed in the electrode and packed by tapping gently on the table top.

Preparation of Standard Curve

A standard curve (Figure 2) is prepared as follows: Each concentration of the standard

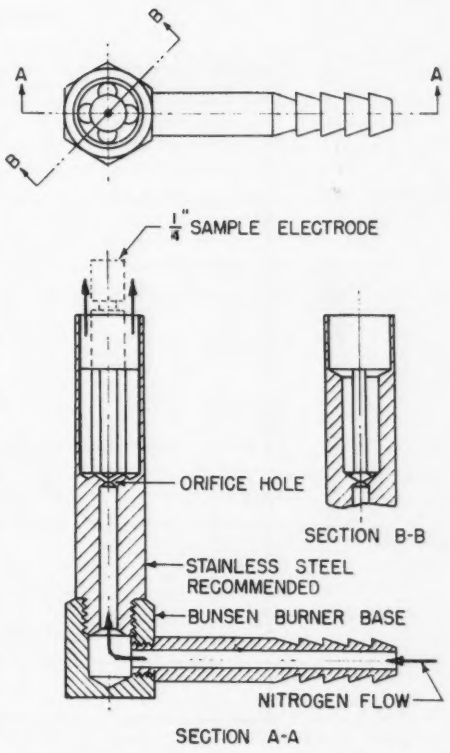

FIGURE 1. Drawing to show the details of construction of the sample electrode holder.

curve is run in triplicate and an average of these is taken for calculation. First, 0.5 ml of internal standard working solution (30 micrograms/0.5 ml) is pipetted into a lead-free 10-ml volumetric flask, followed by 0.5 ml of a lead solution containing 0.2 micrograms Pb/0.5 ml. A series of volumetric flasks is prepared, each flask containing the same amount of internal standard with increasing amounts of lead. The range of the standard curve is from 0.02 mg Pb/liter urine to 0.3 mg Pb/liter urine. After the proper addition of internal standard and lead solutions, the volumetric flask is brought to the 10 ml mark with urine from a person who has not been occupationally exposed to lead. Then 0.1 ml is pipetted from the volumetric flask into an electrode prepared as described above and placed in an oven at 60°C for at least thirty minutes. The temperature is then increased to 105°C and maintained at least one hour. The standards are now ready for analysis. For further explanation see section entitled Spectrographic Procedure.

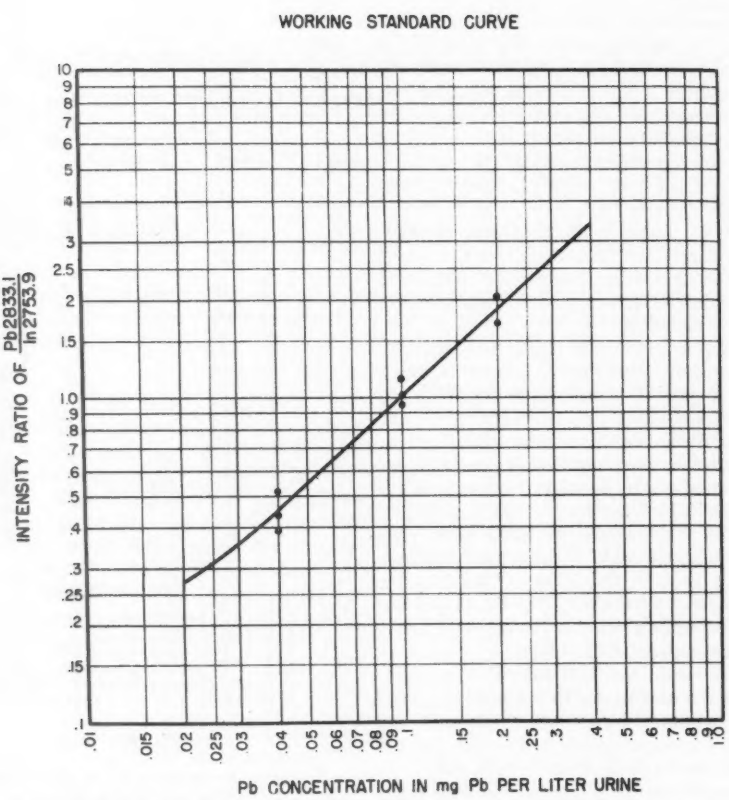

FIGURE 2. Standard curve for the spectrographic determination of lead in urine.

Preparation of Sample

The procedure for preparing a urine sample for analysis is as follows: 0.5 ml of internal standard working solution (30 micrograms/0.5 ml) is pipetted into a lead-free 10-ml volumetric flask. The sample is brought to volume with the urine to be analyzed. Then 0.1 ml is pipetted from the volumetric flask into an electrode prepared as described above. The electrodes are then placed in an oven at 60°C and allowed to dry for at least thirty minutes. The temperature is increased to 105°C and maintained at that temperature for at least one hour. As in the standard curve all sample analyses are run in triplicate and an average is taken for calculation. The samples are now ready for analysis as described below.

Spectrographic Procedure

The spectrograph settings and exposure conditions have been discussed in a previous section.

TABLE I

Urine Samples Run on Spectrograph Containing Added Known Amounts of Lead

Sample No.	mg Pb per liter urine		Deviation
	Added	Found	
1	.13	.14	+.01
2	.17	.18	+.01
3	.08	.09	+.01
4	.11	.08	−.03
5	.17	.20	+.03
6	.07	.08	+.01
7	.04	.04	.00
8	.20	.20	.00
9	.10	.10	.00
10	.218	.20	−.02
11	.000	.03	+.03
12	.007	.02	+.01
13	.158	.15	−.01
14	.106	.12	+.01
15	.027	.05	+.02
16	.04	.05	+.01
17	.053	.06	+.01

After the electrodes have been removed from the oven at 105°C, they are placed in the arc-stand and arced for 24 seconds with the shutter being left open during the entire exposure time. The plate is then developed, fixed and washed at 68°F and dried in the developing machine as previously discussed. The percentage transmittance values of the Pb 2833.1 and In 2753.9 A lines and of the background adjacent to the lead line are determined with the densitometer. The intensity ratios of Pb 2833.1 versus In 2753.9 (with background correction) are established by use of an emulsion calibration curve obtained by the two-step filter method. The concentration of lead is estimated from the working standard curve.

Accuracy

The accuracy of the method was determined first by its ability to recover known amounts of lead added to a single urine specimen. A series of 17 samples was prepared by a chemist other than the spectrographer to permit unbiased analysis. Table I shows the amount of added lead in mg per liter urine, the amount of lead reported found in mg per liter urine, and the deviation of analytical results from the known. The average deviation is plus or minus 0.013 mg lead per liter urine with a maximum deviation of plus or minus 0.03 mg lead per liter urine.

The second procedure used for checking the accuracy of the method was a comparative analysis with a dithizone method used in our laboratory for many years.[5] To compare the spectrochemical method with the chemical analysis, a series of 90 urine samples collected for occupational exposures were run by both methods. The average deviation was 0.017 mg lead per liter urine with a maximum deviation of 0.05 mg lead per liter urine which falls within the confidence level established by analysis of "knowns" as discussed above. The median deviation for the series of 90 urine samples was 0.01 mg lead per liter urine.

Summary

The use of the Emission Spectrograph gives the industrial hygiene laboratory the sensitivity and reliability required for this analysis as well as the flexibility of running a single sample or large numbers of determinations with minimal man-hours per specimen. The ability to determine lead in urine without ashing the urine shortens the time for analysis and reduces the possibility of contamination. The use of the nitrogen atmosphere in the analytical gap serves to lower the spectral background on the plate and to minimize the wandering of the arc around the rim of the electrode. In selecting indium as an internal standard in preference to bismuth we feel confident the possibility of having any residual internal standard in the sample is remote.

Acknowledgment

The authors wish to acknowledge the advice and assistance of Robert G. Keenan, U. S. Public Health Service and also the help given by Morgan D. Carter, Chemist, Michigan Department of Health and Robert C. Bennett, Draftsman, Michigan Department of Health.

References

1. Cholak, J.: Quantitative Spectrographic Determination of Lead in Biological Material. *Ind. and Eng. Chem. (Anal. Ed.) 7:* 287 (1935).
2. Cholak, J., and R. V. Story: Spectrographic Analysis of Biological Material. *Ind. and Eng. Chem. (Anal. Ed.) 10:* 619 (1938).
3. Cholak, J., and R. V. Story: Spectrochemical Determination of Trace Metals in Biological Material. *J. Optical Soc. Am. 31:* 730 (1941).
4. Cholak, J., and R. V. Story: Corrections for Residual Impurity and Background in Spectrochemical Analysis. *J. Optical Soc. Am. 32:* 502 (1942).
5. Hubbard, Donald M.: A Photometric Dithizone Method for Determination of Lead in Biological Material. *Ind. and Eng. Chem. (Anal. Ed.) 9:* 493 (1937).
6. Keenan, Robert G., and John F. Kopp: Spectrochemical Determination of Trace Quantities of Cobalt in Animal Tissues. *Anal. Chem. 28:* 185 (1956).
7. Kumler, K., and T. P. Schreiber: A Rapid Method for Spectrochemical Analysis of Lead in Blood. *Am. Ind. Hyg. Assoc. Quart. 16:* 4 (1955).

Simplified One Color Dithizone Method for Lead in Urine

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By substitution of alpha naphtholphthalein as the indicator instead of phenol red and the use of a single Mojonnier extraction tube or Jacobs-Singer separatory flask instead of multiple separatory funnels, the manipulative steps of the one color dithizone method for lead are simplified and improved.

Introduction

INTEREST in the absorption and excretion of lead has remained at high level for many years. Recently additional interest has been displayed because of many instances of lead poisoning in children.[1] One would think that with the numerous methods for determining lead in biological materials, there would be no need for another, but despite these many methods there is still marked dissatisfaction with them.

The literature concerning the determination of lead in biological materials has been covered in the booklet *Methods for Determining Lead in Air and in Biological Materials*,[2] by Sandell,[3] and by Jacobs[4] and need not be repeated here. One must, however, mention the rapid methods of Woessner and Cholak,[5] of Amdur,[6] and of Bessman and Layne.[7] In general these methods are either spectrographic, polarographic, or dithizone methods, with the latter being used in several variations, namely, mixed color, titrimetric, or one color procedures. The one color method of Fischer and Leopoldi[8] was modified by Harrold, Meek and Holden[9] and subsequently by others. We have modified the one color variation by substitution of alpha naphtholphthalein instead of phenol red as the indicator, the use of a single Mojonnier extraction tube instead of multiple separatory funnels, the addition of fixed amounts of dithizone extraction solution, and the use of filter paper instead of cotton to get a final clear solution for reading in the spectrophotometer. By these changes the one color method has been greatly simplified and possibly improved. Some of the reagents employed are those suggested by Horwitt and Cowgill[10] and by Moskowitz and Burke.[11]

These studies were supported in part by a grant from the National Institutes of Health, U.S. Public Health Service, Department of Health, Education and Welfare.

Equipment and Reagents

Apparatus

A Bausch and Lomb Spectronic 340 was used as the spectrophotometer. Readings were made using 1-inch diameter cuvettes.

The Mojonnier extraction flask (Figure 1) used was their G3A model which has a capacity of 104.5 ml in the top chamber and 21.5 ml in the bottom chamber and is stoppered with a No. 16 pennyhead standard taper glass stopper.

All glassware is washed with dilute nitric acid.

Reagents

Dithizone Solution: Dissolve 50 mg of pure diphenylthiocarbazone in reagent grade chloroform and make up to 500 ml with chloroform.

Ammoniacal Sodium Citrate Solution: Dissolve 100 grams of reagent grade sodium citrate in distilled water and dilute to 500 ml. Add 150 ml of ammonium hydroxide solution (1:1). Mix thoroughly.

Potassium Cyanide Solution, 10%: Dissolve 20 grams of reagent grade KCN in distilled water in a 200-ml volumetric flask and make up to volume with water. Transfer to a reagent bottle and keep in dark, storing it, for instance, in a full metal cabinet. If it becomes discolored discard it and make a fresh solution.

Hydrochloric Acid (1:1): Dilute highest purity hydrochloric acid with an equal volume of distilled water.

Hydroxylamine Hydrochloride, 20%: Dissolve 40 grams of hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, in distilled water and dilute to 200 ml in a volumetric flask. This solution can be purified by shaking out with dithizone extraction solution as detailed by Sandell[3] and by Jacobs and co-workers.[12]

Ammonium Hydroxide Solution (1:1): Dilute

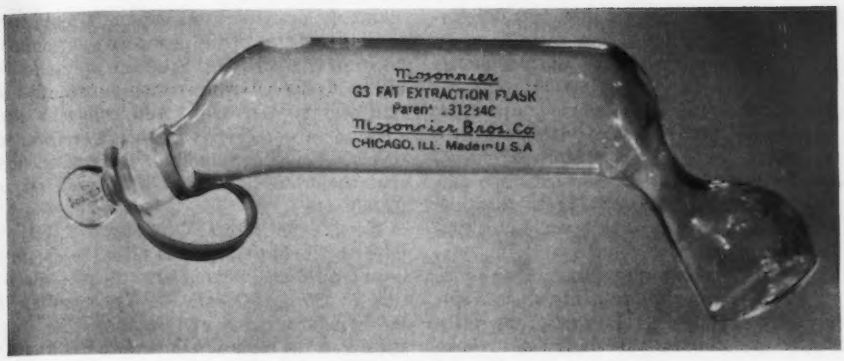

FIGURE 1. Glass-stoppered Mojonnier extraction tube.

one volume of concentrated ammonium hydroxide solution, specific gravity 0.90 with an equal volume of distilled water.

Dithizone Extractive Solution: Transfer 5 ml of 10% potassium cyanide solution and 15 ml of concentrated ammonium hydroxide solution to a 500-ml volumetric flask and dilute to the mark with distilled water.

Indicator Solution: Weigh out 100 mg of alpha naphtholphthalein (National Aniline No. 249) and transfer to a 20-ml beaker. Add 10 ml of distilled water and stir to wet the indicator. Add 4 ml of 0.01*N* sodium hydroxide solution. The indicator dissolves to form a deep blue solution. Transfer to a 250-ml volumetric flask, wash the beaker thoroughly with water and transfer the washings to volumetric flask. Add an additional 6 ml of 0.01*N* sodium hydroxide solution, make to the mark with distilled water, stopper and mix thoroughly. This is a 0.04% solution of alpha naphtholphthalein. It is virtually colorless in acid solution and changes to a green to blue green at pH 8.

Standard Solutions

Stock Standard Lead Solution: Weigh out accurately 1.598 g of recrystallized lead nitrate, $Pb(NO_3)_2$, transfer to a one-liter volumetric flask. Dissolve in 0.1% nitric acid and make to the mark with this acid. One milliliter of this solution contains one mg of lead.

Standard Working Lead Solutions: Transfer one ml of this stock standard solution to a 100-ml volumetric flask and dilute to volume with distilled water. This solution contains 10 micrograms per milliliter. Transfer 10 ml of this dilution to a 100-ml volumetric flask and dilute to volume. This final dilution contains one microgram per milliliter.

Standard Curve

Transfer with the aid of pipettes 0, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 10.0, and 15.0 ml of the one microgram per milliliter working standard solution to 100-ml volumetric flasks. These volumes are equivalent to 0, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 10.0, and 15.0 micrograms of lead, respectively. Add 15 ml of hydrochloric acid and continue with the method as detailed in the procedure but omit the heating steps. Place the final chloroform solution in one-inch tube cuvettes and read in the Bausch and Lomb spectrophotometer at 525 mμ. Plot the micrograms of lead against the transmission. The average of several standard runs is plotted in Figure 2.

Procedure

Transfer 50 ml of urine to a Coors porcelain casserole size 180-3A and evaporate cautiously on a hot plate in a hood to dryness using low heat at first. After the urine has been evaporated continue heating on the hot plate at high heat until the material chars. Transfer the casserole to a muffle furnace that has been adjusted to 550°C and heat at that temperature for 10 minutes. Remove the casserole from the furnace and allow to cool. Add two ml of concentrated nitric acid and replace it on the hot plate in the hood and drive off the nitrogen oxides. Replace in the muffle furnace at 550°C and again heat for 10 minutes. Do not permit the temperature to rise above this. Remove from the muffle furnace, allow to cool, add 15 ml of hydrochloric acid to the casserole washing the sides with the acid, heat on the hot plate and transfer to a 100-ml volumetric flask. Add 10 ml of distilled water to the casserole washing the sides of the dish with the water, heat on the hot plate, and transfer to the 100-ml volumetric flask. Repeat this step

using 15 ml of ammoniacal sodium citrate solution. Repeat the washing again with 10 ml of water and add the washing to the volumetric flask.

Allow the flask to cool to room temperature and add one ml of 20% hydroxylamine hydrochloride solution and 0.5 ml of alpha naphtholphthalein indicator solution. Add sufficient ammonium hydroxide solution (1:1) to turn the indicator blue. Add 5 ml of 10% potassium cyanide solution and make to volume.

Place 10 ml of chloroform solution in a Mojonnier tube and transfer the contents of the volumetric flask to the tube. Add 0.2 ml of the dithizone solution, stopper the flask, and shake thoroughly, holding the stopper firmly. Set upright and release the stopper cautiously. Add additional volumes of dithizone solution 0.1 ml at a time, shaking after each addition until the chloroform layer turns purple. Allow to stand until the phases separate. Pour off the supernatant solution to the constriction and discard. Add an additional 10 ml of chloroform and discard most of the remainder of the aqueous layer.

Add 10 ml of potassium cyanide-ammonium hydroxide extractive solution, stopper the tube, shake, and allow to separate. Pour off the supernatant as before, Repeat by adding an additional 10 ml of this extractive solution. (If care is exercised in addition of the dithizone solution so that not too large an excess is added, only two washings with the cyanide-ammonia extractive solution will be required.) Add sufficient chloroform to raise the level of the chloroform layer to just above the middle of the constriction so that the water layer can be poured off completely.

Wet a 9- or 11-cm. Whatman No. 41H filter paper with chloroform and filter the chloroform layer into a one-inch cuvette. Read the absorption at 525 mμ. Obtain the concentration from the standard curve and compute the concentration on the basis of micrograms per liter.

Results

The results obtained with several series of standard curves are shown as an average standard curve in Figure 2. It can be seen by reference to this curve that 0.2 microgram of lead can be read with ease.

Representative recoveries of lead added to urines are the following: Added 1.0, 2.0, 3.0, 5.0, and 8.0 micrograms; found 1.5, 2.6, 3.0, 5.1, and 7.6 micrograms respectively. These show adequate recovery of lead by this method.

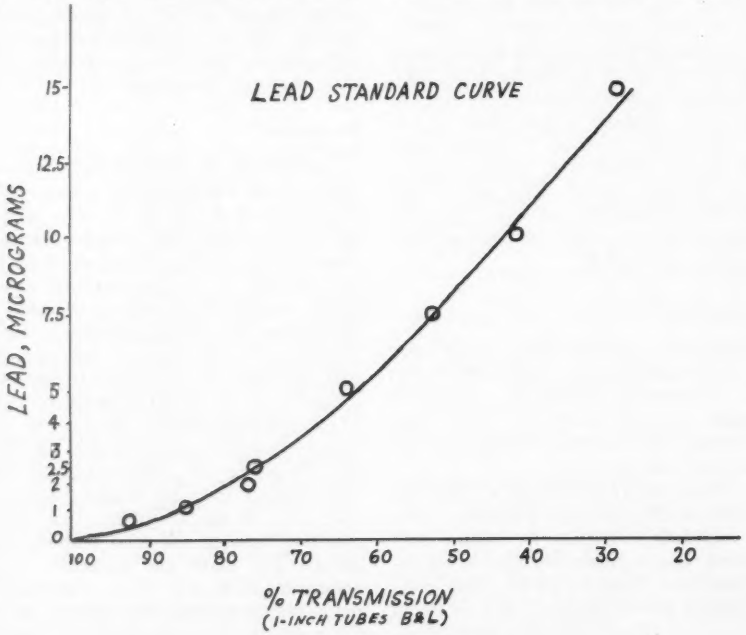

FIGURE 2. Standard curve.

Discussion

The many variations of the mixed color as well as the one color dithizone methods indicate that difficulty is encountered in their use. The errors in these methods have been discussed by Sandell.[3] With particular respect to the one color method, possibly the greatest disadvantage has been the need for using multiple banks of separatory funnels. Not only did this increase the amount of glassware to be washed but at each transfer there was some likelihood that some chloroform extract is lost. With the use of the Mojonnier extraction tube or the Jacobs-Singer separatory flask any number of washings can be performed with the same vessel. If more than 100 ml of test sample is to be extracted then 100-ml or smaller aliquots can be shaken out and each supernatant discarded. In pouring off the final washing, a drop or two of the aqueous layer may remain. This will be removed in the filtration. If one selects to pour off all the aqueous layer and with it a drop or two of the final chloroform solution, the resultant error will still be less than the losses encountered in the repetitive transfers from separatory funnel to separatory funnel.

Although phenol red is almost universally used to set the proper pH for the extraction of lead, we found it unsatisfactory. Indeed, in the ashing method when the indicator is first added to the acid solution, a reddish color is obtained even after the addition of a small volume of ammonium hydroxide solution and an inexperienced analyst might be misled and think that neutrality had been reached. This is dangerous since the potassium cyanide solution might be added while the solution was still acid. The color of phenol red actually goes from reddish to yellow to red. We thought that the use of alpha naphtholphthalein might be an improvement and we found that it was, for the indicator is virtually colorless on the acid side and then becomes green to blue green without any intermediate indeterminate color on the alkaline side. Thus danger in the addition of cyanide is minimized.

Customary directions call for filtration through a pledget of cotton. In our experience this often gave cloudy solutions. By filtering our final extract through Whatman No. 41H filters we invariably obtain clear solutions.

It is known that some lead may be lost with repeated washings of the lead dithizonate in chloroform. We have attempted to minimize this source of error by adding the least excess possible so that only two or at the most three washings of the chloroform layer are required. Adding the dithizone solution in increments of 0.1 to 0.2 ml helps to control this aspect as well as experience with the method. The Mojonnier tube and the Jacobs-Singer separatory flask are helpful here too, for sighting through the chloroform layer in these flasks to evaluate the color change is better than sighting through a separatory funnel.

Although this method is not designed primarily as a rapid method in contrast to those methods cited in the introductory section, it is to be noted that the ashing step itself is relatively rapid and does not take over 25 to 30 minutes. Ten minutes are needed for the first ignition; 5 to 10 minutes for the cooling, addition of nitric acid, and heating on the hot plate to drive off the nitrous fumes. In effect, it is no longer than the many manipulative steps of precipitation, centrifugation, washing, and resolution of the rapid methods. Furthermore in the ashing step the lead in organic combination or held by chelating agents is recovered completely. By igniting the second crucible while the first is cooling, one can speed up the determinations even with a small muffle furnace.

By use of one-inch tubes as little as 0.20 microgram can easily be read and less than that may be approximated. This means that one may use less than 50 ml of urine as the sample.

The method, virtually without change, has been used for blood and spinal fluid. Blood requires an additional treatment with nitric acid and reignition. The ability to read as little as 0.2 microgram enables the analyst to use as little as 4 ml of blood and 2 ml of spinal fluid.

Summary

Lead in urine is determined by ashing the urine, dissolving the ash in hydrochloric acid and ammoniacal sodium citrate, adjusting the pH to 8 with ammonium hydroxide using alpha naphtholphathalein as the indicator which goes from virtually colorless to green blue, extracting with a chloroform solution of dithizone with the aid of a Mojonnier extraction tube to avoid the use of multiple separatory funnels, washing out the excess dithizone with cyanide-ammonia solution, filtering the chloroform layer to obtain a clear solution, and reading the amount of lead dithizonate at 525 mμ with one-inch cuvettes. This one color dithizone method is simple, relatively rapid, and overcomes many of the disadvantages of other variations. The method is adequate for 0.25 microgram of lead.

References

1. KAPLAN, E., AND R. S. SHAULL: Determination of Lead in Paint Scrapings as an Aid in the Control of Lead Paint Poisoning in Young Children. *Am. J. Public Health 51:* 65 (1961).
2. *Methods for Determining Lead in Air and Biological Materials.* 2nd Ed., Am. Public Health Assoc., New York (1955).
3. SANDELL, E. B.: *Colorimetric Determination of Traces of Metals.* 2nd Ed., Interscience Publishers, New York (1950).
4. JACOBS, M. B.: *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents.* 2nd Ed., Interscience Publishers, New York (1949).
5. WOESSNER, W. W., AND J. CHOLAK: Improvements in the Rapid Screening Method for Lead in Urine. *AMA Arch. Ind. Hyg. 7:* 249 (1953).
6. AMDUR, M. O.: Rapid Determination of Lead in Old Urine Samples. *AMA Arch. Ind. Hyg. 7:* 277 (1953).
7. BESSMAN, S. P., AND E. C. LAYNE, JR.: A Rapid Procedure for the Determination of Lead in Blood or Urine in the Presence of Organic Chelating Agents. *J. Lab. Clin. Med. 45:* 159 (1955).
8. FISCHER, H., AND G. LEOPOLDI: Colorimetrische Bestimmung von Blei und Kupfer mit Dithizon. *Angew. Chem. 47:* 90 (1934).
9. HARROLD, G. C., S. F. MEEK, AND F. R. HOLDEN: A Practical Method for the Rapid Determination of Lead when found in the Atmosphere. *J. Ind. Hyg. Toxicol. 18:* 724 (1936).
10. HORWITT, M. K., AND G. R. COWGILL: A Titrimetric Method for the Quantitative Estimation of Lead in Biological Materials. *J. Biol. Chem. 119:* 553 (1937).
11. MOSKOWITZ, S., AND W. J. BURKE: Method for the Analysis of Dust and Fumes for Lead and Zinc. *J. Ind. Hyg. Toxicol. 20:* 457 (1938).
12. JACOBS, M. B., S. YAMAGUCHI, L. J. GOLDWATER, AND H. GILBERT: Determination of Mercury in Blood. *J. Am. Ind. Hyg. Assoc. 21:* 475 (1960).

RUSSIAN AIR POLLUTION LITERATURE

THE U.S. DEPARTMENT OF COMMERCE, Office of Technical Services, has announced the publication of the fifth volume in a continuing survey of Russian literature on air pollution and related occupational diseases, being conducted by Dr. Ben S. Levine under a U.S. Public Health Service research grant. This survey of Soviet literature dealing with the air pollution aspects of industrial and public health problems contains translations of 45 articles in six sections dealing with: Russian studies of limits of allowable concentration; pharmacological, toxicological, and clinical data; industrial sanitation; ionization and ultraviolet radiation; benzpyrene; and analytical techniques for measuring various pollutants. Dr. Levine has included an analysis of Pavlovian physiology and its potential use in investigations of air pollution in his introduction to Volume 5. This continuing survey series covers concepts which form the basis of air pollution prevention in the USSR, explains the methods of approach, outlines the scope and plan of the work, and evaluation of the progress made.

Two translations have been published in 1961 and are available for purchase from the Office of Technical Services, Business and Defense Services Administration, U.S. Department of Commerce, Washington 25, D.C. The two publications are:

61-11149 *USSR Literature on Air Pollution and Related Occupational Diseases.* Volume 5. January 1961. 219 pages. $3.50.

61-11148 *Limits of Allowable Concentrations of Atmospheric Pollutants.* Book 4. $2.75.

A Practical Stack Sampling Procedure

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A practical stack gas sampling procedure applicable to most field conditions is described. Metering, sampling and analytical variations provide the versatility needed. Several tables are suggested as field work aids to the engineers. Particulate loading of filters, mass-emission-rates, collection efficiencies, and calibrations are discussed.

Introduction

A PRACTICABLE stack sampling procedure has been developed and used during the past ten years by the Industrial Hygiene Department of the General Motors Corporation. The procedure is fundamentally based on established practices.[1, 2]

Recognizing that ideal stack sampling conditions seldom exist in plant installations, effort has been made to minimize the effect of those shortcomings which tend to oppose the attainment of representative samples. To gain necessary versatility, variations have been introduced in metering, sampling and analytical techniques. These changes have enabled reasonable particulate loading, mass-emission-rate and dust-removal-efficiency determinations to be made in a wide range of circumstances.

Selection of Sampling Locations

The selection of sampling locations is almost invariably a compromise with the ideal. Individual judgement must be made in each situation as to which possible location affords opportunity for the greatest accuracy in velocity pressure measurements and representativeness in subsequent sampling.

Having made this choice, sampling ports are usually prepared by means of a rotating hole saw of either 1.5 or 2.5 inch diameter. The 1.5-inch hole accommodates the sampling probe of a wet train, but a 2.5-inch hole is required when filter thimbles are used. The larger hole is needed for a dry train because the entire integral-head thimble holder is positioned in the contaminated air or gas stream.

Occasionally, the best sampling location is judged to be just over the rim of a discharge stack, as shown in Figure 1.

Sampling Trains and Accessories

In the instance shown, Figure 1, the inlet nozzle of a simple wet-type sampling train is inserted through the discharge stack opening. The probe is secured by a toggle-lock wrench to a support bracket attached to the stack by sheet metal screws. An aluminum rod and clamp assembly holds an all-glass standard impinger to the stainless steel probe. This particular probe has to be held by hand, however, for traverse points close to the near side of the stack. Amber latex hose of ½-inch inside diameter and 3/16-inch wall thickness has proved highly satisfactory for conducting air or gas to the sampling pump.

The pump and some of its orifice-meter features are shown in Figure 2(A). A vacuum gauge for measuring pressure on the up-stream side of the orifice flow meter is located at the top left. Just to its right is the flow meter which consists of a Magnehelic gauge, with a differential pressure range of 0 to 12 inches of water, and a 3/16-inch sharp-edge orifice plate. The orifice plate is mounted in an ordinary ¼-inch cast iron union with nipples on either side for gauge connections. An air bleeder valve for regulating air flow is located below the union.

Another view of the pump assembly, Figure 2(B), shows its electrical features. These include an on-off switch, and both male and female three-wire Hubbell connectors. The connectors permit series-connections between two or more pumps where it is not convenient to have separate power leads.

And, for convenience, aluminum cases have been arranged so the box top can serve as a low table, as shown in Figure 2(C).

As an added feature, the top has two gauge windows and a hinged door in one end, Figure 2(D), so the top does not actually have to be removed in order to operate the pump. Figure 3 illustrates the pump box being used in this manner. Note also the rod and clamp support of the sampling train, which in this case is a dry train with the thimble and holder completely inside the stack.

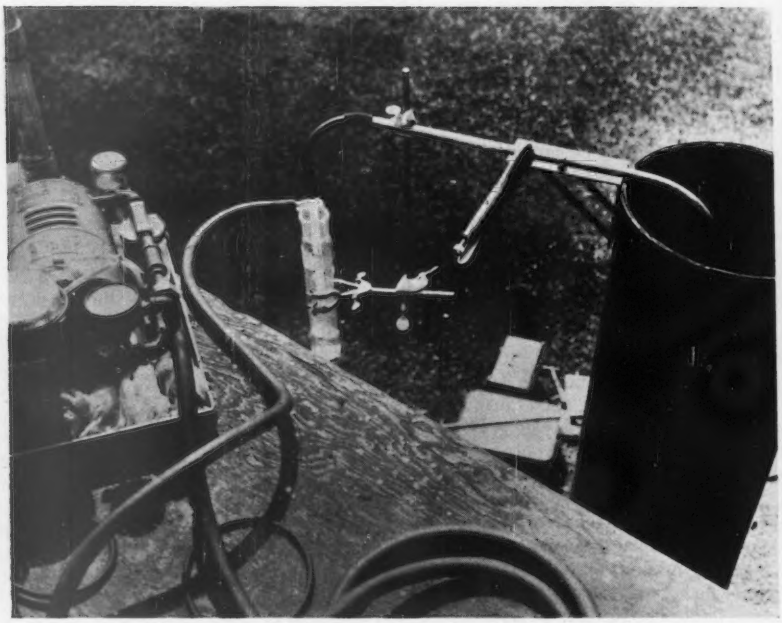

FIGURE 1. A simple wet train.

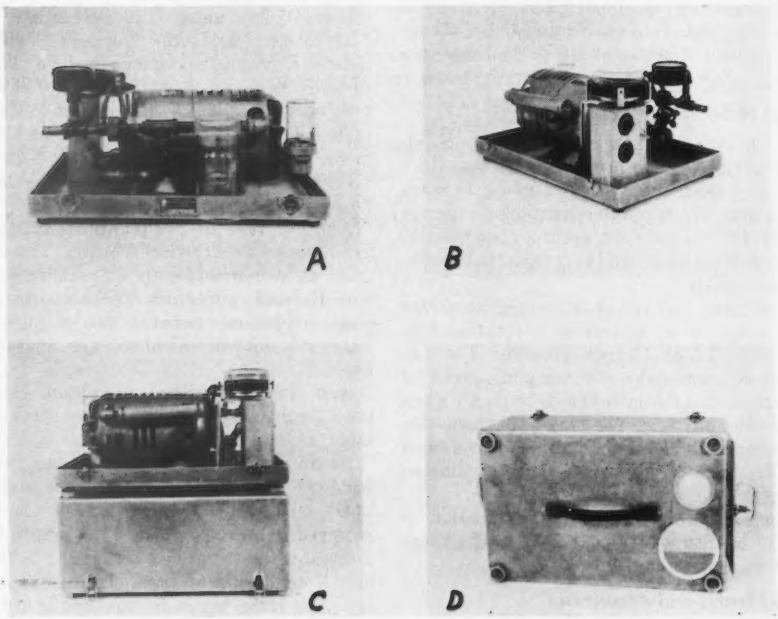

FIGURE 2. Sample pump and orifice flow meter, showing: (a) flow meter and control valve; (b) electrical features; (c) box top used as small table, and (d) windows and door in box top.

FIGURE 3. Dry sampling train, with thimble holder in stack.

References have been made to sampling trains, which are designated as "wet" or "dry". The dry train includes an aluminum integral-head thimble holder, Figure 4, with a short, straight, orifice nozzle tube and a weighed paper thimble. The holder is connected by a 90° elbow to a supporting length of ⅜-inch pipe. The pipe in turn is connected by ½-inch latex hose to one of the flow metering air sampling pumps.

This train is principally used for collecting particulate matter from both not too hot, and cold, air streams. It is only occasionally used in efficiency studies.

The wet sampling train consists of conventional stainless steel probe and nozzle set components, all-glass standard Greenburg-Smith impingers, hose, and metering air pump as above. The sample entrainment medium usually is n-butyl alcohol, but distilled water or various reagents are sometimes used. This train especially is used to collect particulate matter from air streams when particle size information is desired. It has proved to be very good for hot gas, wet and oily work, as well as for more normal sampling. In many cases, the standard impinger is preceded by another impinger with orifice removed from the center tube. The modified tube serves as a primary collector of large particles

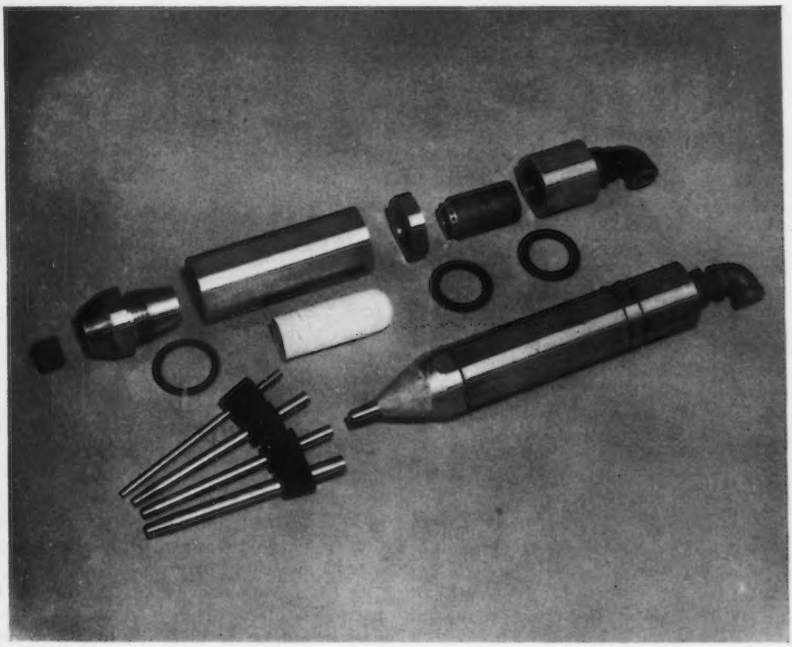

FIGURE 4. Exploded, and assembled view of integral-head thimble holder.

TABLE I

Typical Pre-Calculated 10-Point Traverse Values*
(Distance from wall of round ducts
to center of equal-area zones.)

Diameter in Inches	Distance from End of Pitot and/or Sampling Probe to Point Number									
	1 .026 XD	2 .082 XD	3 .146 XD	4 .226 XD	5 .342 XD	6 .658 XD	7 .774 XD	8 .854 XD	9 .918 XD	10 .974 XD
30	¾	2½	4⅜	6¾	10¼	19¾	23¼	25⅝	27½	29¼
31	¾	2½	4½	7	10⅝	20⅜	24	26½	28½	30¼
32	⅞	2⅝	4⅝	7¼	11	21	24¾	27⅜	29⅜	31⅛
45	1⅛	3¾	6⅝	10¼	15⅜	29⅝	34¾	38⅜	41¼	43⅞
46	1¼	3¾	6¾	10⅜	15¾	30¼	35⅝	39¼	42¼	44¾

* Only a portion of a typical table is given here for purpose of illustration; the complete table would indicate values at all intermediate diameters from 32 to 45, not shown here.

TABLE II

Typical Pre-Calculated Air Flow
and Pump Calibration Data*
(for ¼-inch probe nozzle)

Vp	$Vp^{1/2}$	FPM	Pump CFM	Magnehelic Gauge Readings-Inches of Water					
				Dry: Meter No.			Wet: Meter No.		
				1	2	3	1	2	3
.56	.75	2997	1.02	3.3	3.1	2.7	3.6	3.2	2.9
.57	.75	3024	1.03	3.4	3.2	2.8	3.6	3.3	2.9
.58	.76	3050	1.04	3.4	3.2	2.8	3.7	3.4	3.0
1.06	1.03	4123	1.41	6.3	6.0	5.2	—	—	—
1.07	1.03	4142	1.41	6.3	6.0	5.2	—	—	—

* Only a portion of a typical table is given here for purpose of illustration; the complete table would contain all intermediate values from 0.58 to 1.06, not shown here.

to prevent blockage of the standard impinger orifice.

Although the wet procedure is the more versatile, it also necessitates more work both in the field and in the laboratory. Each probe component must be carefully wet-brushed and rinsed into the sample flask. Acetone is used as a final rinse in the field to assure clean, dry, probe sections for each succeeding use. Quantitative transfer from each flask is necessary in the laboratory.

Work Aids

Appropriate tables have been prepared to minimize field calculations as much as possible.

Included in the field engineer's notebook are pre-calculated 4-, 6-, 8-, 10- and 12-point traverse tables for round pipe. In the 10-point traverse, illustrated by Table I, stack inside diameters are given in the column at the left. Successive numbers toward the right are the distances to be marked off from a center line through the entrance leg of both the pitot tube and the sampling probe. Both instruments, subsequently, are consecutively positioned with these markings at the inside edge of the stack. For pipe sizes not included, underscored multiplying factors are given at the top of each column.

We have not prepared this type of information for rectangular stacks because fewer of these are encountered, their range of sizes is greater, and the related equal-area center calculations are much less difficult to compute in the field.

The second work aid, illustrated by Table II, combines pump calibration data with air flow measurements. Under some circumstances the Magnehelic gauge readings given in the six columns at the right depend only on the stack velocity pressure readings given in the first column at the left. Using a ¼-inch probe nozzle, these gauge readings assure isokinetic sampling under standard conditions. A wet or dry sampling train, and any of three orifice flow meters may be used.

The sampling rates in standard cfm are indicated in the fourth column, and the stack velocities in fpm are given in the third column. For convenience, the square roots of velocity pressure values are given in the second column.

Whenever gas temperature varies by as much as 25 degrees from 70°F, or absolute stack pressure varies by as much as one inch from 29.9 inches of mercury, the procedure is more complex. This is also true if a nozzle size larger than ¼-inch is used in order to sample at a higher rate, as is often done. The more complex procedure will be subsequently described. In any event, the last six columns represent direct calibration data for the standard cfm sampling rates shown in the fourth column. They fail to apply only when flow resistance up-stream of the orifice meter exceeds certain limits during sampling. Reference must then be made to base calibration curves and Magnehelic gauge readings varied accordingly.

A third work aid, Table III, consists of two parts. The first part is a list of available probe sizes including the cross-sectional area for each,

expressed in 10^{-5} square feet. The second part is a transitional air flow formula which enables determination of (a) the largest usable probe nozzle size, and (b) the necessary standard cfm at the pump required for each traverse point. In this formula, standard cfm at the pump is equal to 17.7 times Vo (the stack velocity in fpm at a point) times the ratio of absolute pressure to absolute temperature, times the cross-sectional (C.S.) area of the probe nozzle.

In its first use, to determine which probe nozzle to use, consideration is given the highest practical sampling rate (say 1.3 cfm for a wet train and two cfm for a dry train) and the maximum value of Vo in a given traverse. Solving for C.S. area of probe nozzle indicates the largest size that can be used.

The formula is then used to determine the cfm at the pump for each traverse point. This is done in a straight-forward manner using successive Vo values.

Data Sheets

Measurements and observations are recorded on a data sheet as shown in Figure 5. Thirty-six pound ledger bond has proved to be especially suitable because this grade of paper has firm body, does not tear easily and is resistant to wetting and soiling effects that are frequently encountered.

The data sheets have been designed to facilitate development of the various steps included in the sampling procedure. All of the information shown on the data sheet generally proves useful. This information consists of the name and section of the plant, the date of test, simple weather observations, the test and stack numbers, a description of the test location and the system involved, the inside diameter or rectangular stack dimensions, the cross-sectional area, and the gas temperature in degrees Fahrenheit and Absolute.

The absolute pressure (PA) in the stack is determined by adding to the barometric pressure (PB), as measured with an aneroid barometer, the static pressure (SP) in commensurate units. Fv, which we call a velocity factor, is calculated by taking the square root of the ratio of the absolute temperature to the absolute pressure and multiplying by 952.6. This factor includes all basic elements of gas flow formulation important to this procedure, except velocity pressure. It is used subsequently in computing stack gas velocities.

Center of equal-area traverse distances is entered under "Location" in the body of the data sheet. These distances are also marked off from

TABLE III

Probe Nozzle Dimensions and Formula for Determination of CFM at Pump

Probe and Nozzle Types Available				I.D. (inches) at Leading Edge		C.S. Area at Leading Edge $\times 10^{-5}$ sq. ft.
Nozzle sets	Steel tubes	Goose necks	Glass tubes	Common fraction	Decimal equiv.	
X	X	X		3/16	.188	18.2
X				13/64	.204	22.6
X		X		7/32	.219	26.0
X				15/64	.235	30.0
X	X		X	1/4	.250	34.0
X				9/32	.292	46.5
X	X	X	X	5/16	.313	53.2
X				11/32	.344	64.3
X	X	X	X	3/8	.375	76.3
X				7/16	.437	104
X		X	X	1/2	.500	136
X				9/16	.562	172
		X		5/8	.623	211
			X		.650	229

CFM (Std.) at Pump

$$= \text{C.S Area} \times \text{Vo} \times \frac{530}{460 + t} \times \frac{\text{PA}}{29.9}$$

$$= 17.7 \times \text{Vo} \times \text{PA/Ts} \times \text{C.S. Area}$$

where:

Vo = FPM in stack at sampling point.
PA = Abs. Pressure, In. Hg., in stack.
Ts = Abs. Temperature, deg. Rankine, in stack.
C.S. Area = Cross Sectional Area of probe nozzle in 10^{-5} sq. ft.

the probe end on a standard pitot tube. Using an inclined manometer, in conjunction with the pitot tube, the velocity pressure is determined at each so-indicated point number of the stack. These values are entered under the column headed, Vp ("H_2O).

If both the absolute temperature and the absolute pressure are near standard, and the range of Vp readings is such that desirable sampling rates are indicated in the ¼-inch nozzle table, all precalculated data may simply be transcribed, including Magnehelic gauge flowmeter readings.

Where non-standard conditions exist, the square root of each velocity pressure reading is multiplied by the velocity factor, Fv, to obtain the velocity, Vo, for each traverse point. Table III is used as previously explained to determine nozzle orifice size and sampling rates. The gauge readings are then transcribed from Table II.

To complete the data sheet, the duration of sampling at each point and the sampled gas volume are entered, the time of beginning and ending the test, and the initials of the test engineer. "Remarks" include production information relating to the test, a list of operations covered and

PLANT OUTLAND, FT. JONES SECTION BODY SHOP DATE 11-2-60

WEATHER FAIR; 70°F; W-10

TEST NO. 7 STACK NO. 371 DESCRIPTION BLOW OUT BOOTH EXHAUST -- AFTER FILTER

I.D. 30 (IN.) A 4.910 (FT^2) TEMP. 75 °F + 460 = 535 (Ts)

PA = 29.48 PB + .05 SP($"H_2O$)/13.6 = 29.5 ("Hg) Fv = $(Ts/PA)^{\frac{1}{2}}$ x 952.6 = 4055

PROBE (I.D.) 1/4 (IN.) A 3.40 x 10^{-5} (FT^2) (DRY) THIMBLE NO. 21-A

FLOWMETER NO. 2 (WET) IMPINGER NO. ---

POINT NO.	LOCATION	Vp ($"H_2O$)	$(Vp)^{\frac{1}{2}}$	Vo (Fv x $Vp^{\frac{1}{2}}$)	CFM (PUMP)	GAUGE ($"H_2O$)	TIME (Min.)	VOL. (STD.) (CFM x Min.)
1.	3/4	.97	.98	3940	1.34	5.4	12	16.1
2.	2-1/2	1.05	1.02	4100	1.40	5.9	12	16.8
3.	4-3/8	1.01	1.00	4020	1.38	5.7	12	16.1
4.	6-3/4	.89	.94	3780	1.29	4.9	12	15.4
5.	10-1/4	.70	.84	3350	1.14	3.8	12	13.7
6.	19-3/4	.57	.75	3020	1.03	3.2	12	12.4
7.	23-1/4	.60	.77	3100	1.06	3.3	12	12.7
8.	25-5/8	.85	.92	3690	1.26	4.7	12	15.1
9.	27-1/2	1.01	1.00	4020	1.38	5.7	12	16.1
10.	29-1/4	1.05	1.02	4100	1.40	5.9	12	16.8
11.								
12.				$\overline{Vo}$ = 3712			TOT =	152.4 C.F.

TIME TEST STARTED 1300 TIME TEST ENDED 1500 TEST RUN BY JH & OJ

REMARKS: LINE SPEED: 32 PASSENGER BODIES PER HR. CONVEYOR DOWN FOR 10 MIN. DURING TEST

LAB. AND CALCULATIONS:

Qo = A x $\overline{Vo}$ = 18,200 CFM (at Ts and PA)

SOLIDS FOUND 1.2 Mg.

Mg. x 0.0154 = .018 GRAINS

$Q_{STD.}$ = Qo x 530/Ts x PA/29.5 = 17800 CFM (at 70°F.)

GRAINS/C.F. (STD.) = .018/152.4 = .000012

1.2x10^{-4} GRAINS/C.F.-STD. x 17800 $Q_{STD.}$ x 60/7000 = 0.018 LBS./HR.

FIGURE 5. Sample data sheet.

all individual observations that might have any bearing on the results.

Although stack gas volumes may be calculated in the field, all remaining calculations are necessarily reserved until laboratory work has been completed. Then for particulate matter, the weight of solids found is progressively computed in grains per cubic foot and pounds per hour. Other calculations pertaining to particle size data and chemical analyses may be made on the reverse side of the data sheet. By use of the data sheet in the manner described, all information pertaining to a given test is thus confined to a single location.

Sampling

It seems appropriate to offer a few comments as to how a sampling traverse is made, including the location and duration with respect to its general purpose. A traverse is made by aspirating stack gas through the sampling train while the probe nozzle is located at each traverse point in the stack for a given number of minutes. Unused portions of holes in ductwork, having negative pressure, are closed off during both the velocity and the sampling traverse.

The duration of a sampling traverse will range from less than ½ hour to several hours. The duration depends on the purpose of the test, the apparent dirtiness of the gas stream, the air velocities to be matched and the constancy of dust producing operations. An effort is made to collect at least 300 milligrams of dust in each sample, but as little as 15 or 20 milligrams will suffice in some instances, especially on the clean side of an efficient arrestor.

Whenever efficiency studies are made, simultaneous sampling traverses are made at two or more locations. Repetitive runs are sometimes made, although for general surveys involving a number of stacks, single runs often suffice. A portable field telephone set has proved very helpful as an aid in synchronizing bi-level efficiency tests, or for use between discharge stack sampling personnel on the roof and process personnel in the plant.

Analytical Procedures

A brief review of the analytical procedures applied to the collected samples should promote understanding of our subsequent interpretation of results.

Whatman, 33 x 94 mm, fat extracted, seamless, single paper thimbles are principally used in the dry procedure—alundum thimbles very infrequently. Careful moisture control over laboratory weighing of the paper thimbles is necessary, both before and after use, but with repeated oven-drying, desiccator cooling, and weighing under uniform conditions, weight constancies to less than one milligram are attained.

The contents of standard impingers are transferred, with careful policing and rinsing of the flasks and center-tubes, into previously dried and weighed screen or sieve sets of three inch diameter. The materials are wet-screened by successive washings first with n-butanol and finally with n-pentane to remove oil and promote oven drying. Only two screen sizes are used, of 200 and 325 mesh, with aperture openings of 74 microns and 44 microns, respectively. The washings are evaporated to dryness, after oil extraction in some instances, and the residue weighed. The dried screens are reweighed and three weight fractions based on particle size are thereby attained: over 74 microns, 44 to 74 microns and under 44 microns.

Before evaporation of the washings is begun, the material is thoroughly mixed and a relatively minute aliquot removed for microscopic examination. By means of a light-field technique, entailing the use of Dunn cells and a Whipple disc in the eye-piece, estimate is made of the number of particles in each of several size ranges. Hence, a count distribution is arrived at in the following ranges: 20–44 microns, 10–20 microns, 5–10 microns, and 5 microns or less.

Chemical, spectrographic, Orsat or other analyses are made of collected solids, liquids and gas samples as needed, and titrimetric or other analysis with specific reagents is done in some instances.

The Significance and Justification of Possible Variations

By means of the procedure described and at times under seemingly impractical circumstances, it has been possible to ascertain degrees of compliance with existing regulatory codes, to compare air cleaner performance data for different types of cleaners on given applications, and to further the selection of new and replacement equipment.

Many variables that are often encountered, including temperature, pressure, water vapor, particle size and chemical, aerodynamic and other considerations have limiting effects on any sampling procedure.

Some of the inherent steps and analytical or other concepts that contribute to the over-all ability of this procedure to approach sample "representativeness" may be summarized as follows:

(1) In selecting sampling locations, judgment must be used to make the "best compromise with the ideal". In some cases, however, even a single sampling traverse direction will suffice.

(2) To offset increasingly unfavorable aerodynamic conditions, just as with an increase in cross-sectional area, a correspondingly larger number of equal-area centers should be included in each velocity and sampling traverse.

(3) It is recognized that under highly anisokinetic circumstances, as when extreme turbulence causes complete mixing, representiveness has to be based on homogeneity and related averaging processes.

(4) The sampling rate and probe nozzle orifice sizes are made as large as pump capacities and meter calibrations will permit, and sampling durations sufficiently long to average out the result of process change.

(5) Integral-head filter holders are placed in the gas stream to eliminate impingement in hard to clean right angle inlet probes.

(6) Standard impingers are preceded by modified impingers at times to prolong runs by prior removal of larger particles.

(7) Water vapor is recognized as part of the carrying medium, and with the exception of gas analysis in combustion processes, the results are not put on a dry basis, nor is importance attached to minor changes from normal in the specific gravity of the air or gas usually encountered.

(8) By using orifice flow meters, significant de-

lays in arriving at desired air flows are eliminated.

(9) As collection efficiency nears 100 per cent, where smaller and smaller differences are important, the weight arrested per unit time divided by the corresponding inlet rate approaches unity and sampling error tends to cancel out. In fact, if the same percentage error is made on both sides of a collector, and the sign is unchanged, error in collector efficiency results is nil.

(10) The determination of collection efficiency of a dust arrestor on a per cent by weight basis is of limited value unless particle size distribution is considered. By combining particle size distribution and mass rate data from this procedure, a good picture is obtained as to the degree of arrestance of material: above 74 microns in size, between 44 and 74 microns, and below 44 microns. Count distribution among the less than 44 micron weight grouping is of more limited value. However, the degree to which enrichment of the less than five micron size particles is seen in outlet versus inlet samples reflects a greater arrest of the larger size particles in this particular weight fraction.

Conclusions

The sampling procedure described, although fundamentally based on established procedures, has been aimed at representativeness in sample collection as opposed to isokinetic sampling *per se*.

Metering, sampling and analytical variations were described which provide the versatility and sampling efficiency needed for the attainment of meaningful engineering data. Field efficiency has also been increased by these means, and this has proved to be especially important where systems of numerous types at widespread geographic locations are to be evaluated.

References

1. American Society of Mechanical Engineers; *Test Code for Dust Separating Apparatus.* Test Code 21, American Society of Mechanical Engineers, 29 West 39th Street, New York, New York (1941).
2. *Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases.* Fourth Edition, Bulletin WP-50, Western Precipitation Corporation, 1016 W. Ninth Street, Los Angeles 15, California.

An Air Pollution Control Measure

SECRETARY ABRAHAM RIBICOFF of the U.S. Department of Health, Education, and Welfare praised the General Services Administration for acting to improve Federally purchased motor vehicles in two important ways—requiring seatbelt anchors for passenger safety and positive crankcase ventilation systems, known as "blowby" devices, to reduce the vehicle's contribution to community air pollution. The General Services Administration currently purchases about 7,000 new motor vehicles each year.

Following discussions between the Divisions of Air Pollution and Accident Prevention of the Public Health Service and the Federal Supply Service, the General Services Administration recently issued interim Federal specifications for gasoline-powered vehicles. The amended specifications require positive crankcase ventilation systems for control of "blowby" emissions, and seatbelt anchors suitable for snap-on seatbelt hooks for all 1962 and subsequent models. At present these devices are not standard but are available as optional equipment at extra cost to purchasers desiring them. Crankcase ventilation devices are factory installed by the manufacturers on a voluntary basis on new vehicles delivered this year in the State of California. Secretary Ribicoff has urged their installation at the factory as standard equipment on all new motor vehicles delivered anywhere in this country. The positive crankcase ventilation systems are reported to reduce the total emissions of hydrocarbons in automotive engine exhaust by about 25 per cent at a very nominal cost.

A Study of Beryllium Exposures at a High Explosive Assembly Test Facility

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The firing of explosive assemblies containing beryllium creates a potential hazard of widespread contamination by finely divided and oxidized beryllium. A description of the facilities involved and the results of a study of the degree of contamination are presented. A program of personal hygiene and facility housekeeping for the protection of workers from beryllium contamination is described.

THE use of beryllium metal is continually expanding. There are many articles in the literature relating to the uses, control, and toxicity of beryllium and its compounds. Few studies have been reported which are concerned with widespread contamination out of doors. The increased use of beryllium metal in space vehicles creates a need for this type of information. The static testing of rocket motors usually takes place out-of-doors and in relatively remote areas. Testing rocket motors which have beryllium components may result in widespread contamination.

This is a report of industrial hygiene problems associated with the operation of a high explosive assembly test facility wherein large numbers of beryllium metal assemblies have been detonated. This situation in certain aspects simulates anticipated problems in rocket motor testing.

Test Facility

The high explosive assembly test facility of the University of California Lawrence Radiation Laboratory (UCRL) is located in San Joaquin County approximately fifteen miles east of Livermore and eight miles west of Tracy, California. The terrain is hilly and dry; yearly rainfall is approximately 12 to 15 inches; temperature ranges from 18°F in the winter to 110°F in the summer, and the wind direction is predominantly from the southwest.

Concrete structures (bunkers), illustrated in Figure 1, are used to house diagnostic equipment and personnel. A typical bunker measures approximately 75 ft x 55 ft. Each bunker is air-conditioned and pressurized with respect to the outside air. All air supplied to the bunker is filtered using absolute filters. Air changes occur at a rate of three to four times per hour.

Functions at this site can be divided into four major activities: test firing of high explosive assemblies, high explosive processing and fabrication, process development, and related support research.[1]

Data from three bunkers are mentioned in the report. The activities carried on at each of these bunkers are as follows:

Bunker 301 is equipped to use high speed cameras to record events following detonation of high explosive assemblies.

Bunker 302 obtains the same type of information by use of electronic equipment.

Bunker 312 is equipped with a linear accelerator that produces high energy x rays, which also serves as part of the test equipment.

For the past five years test firing of high explosive test assemblies has been conducted at this facility. During this period several tons of beryllium metal have been included in the high explosive assemblies. Beryllium metal fired in this manner becomes air-borne in a finely divided and oxidized form.

Sampling Procedure

Sampling of air, soil, coveralls, surfaces, water, and respirators are included in the survey program. Air sampling was accomplished by three devices: breathing zone samplers attached to personnel or held over their shoulder next to the face, historical samplers (24-hour) located at fixed points, and portable samplers which were used inside the bunker. Breathing zone samples on the table were obtained by using a Jacobson Hi-Torque pump with a 1.8 hp motor. The sampling rate was 8 cfm using Whatman TFA #41 filter paper.

High and low volume samplers were used inside the bunker. Locations for sampling within bunkers were selected on the basis of personnel activity and likelihood of intrusion and infiltration due

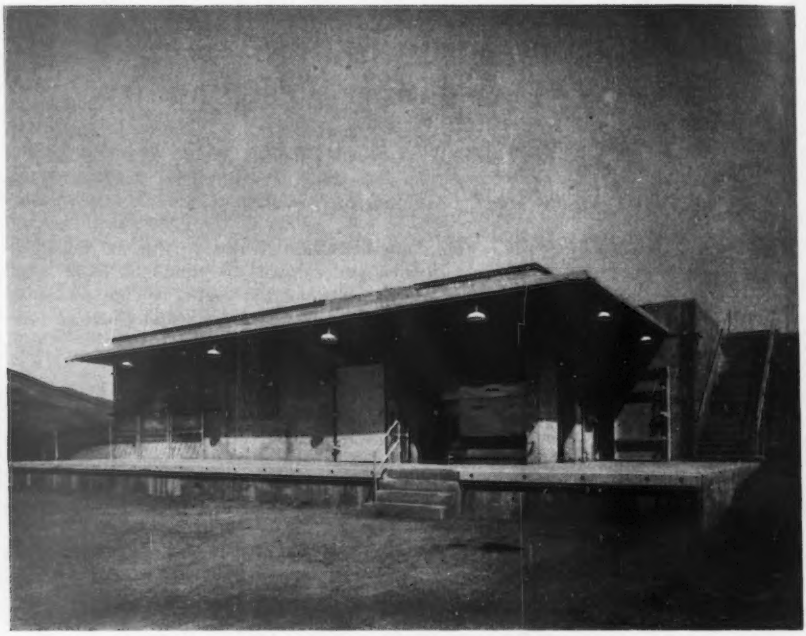

FIGURE 1. Front view of concrete Bunker 302.

to blast conditions. The high volume samplers operated at a rate of 16 cfm; the low volume samplers at 2 and 4 cfm.

Historical samples were obtained from fixed locations within and distant to the test area. These samples were collected for a 24-hour sampling period. All sample papers were changed daily except for a sampler located at Tracy which was changed on a weekly basis.

Firing table soil was analyzed for beryllium at frequent intervals. Approximately 200 to 400 grams of coarse gravel was obtained for each sample. This was sifted through a 325-mesh screen. The sifted material was analyzed for beryllium. Samples were taken at the point of firing and at varying distances outward.

Coveralls worn by personnel who worked on the firing table or in the bunkers were analyzed for beryllium. The wearer's activities were logged with respect to the type of activity the person had engaged in and the time involved. These coveralls were washed by hand in distilled water, and the wash water was analyzed for beryllium. Socks were subjected to the same treatment.

Surfaces inside the bunker were wiped for beryllium. These surfaces include the floor, table tops, walls, overhead pipes, cabinet tops, and other areas suspected of harboring beryllium dust. A typical wipe sample covers an area of 100 cm^2 and is obtained by using an apparatus that marks off the desired dimensions. All samples are taken with filter paper or Kimwipes.

Water samples were routinely collected from the wells which furnish water to the facility. Single-use milk cartons were used as the sampling containers to minimize the possibility of external contamination.

Respirator cartridges were analyzed for beryllium. Cartridges were selected following various personnel activities on the firing table.

Beryllium Analysis

Upon receipt, air, wipe, and liquid samples are acid digested in 80% concentrated nitric and 20% concentrated perchloric acid. The dry 325-mesh fraction from soil samples is oven-dried prior to acid digestion. Respirator cartridges are dry-ashed at 450°C and then acid digested. The acid solution is analyzed for beryllium using the Sill and Willis[2] technique as modified by N. L. Smith of UCRL. The modified procedure is as follows:

Impurities in the acid digest are removed by a beryllium-aluminum co-precipitation in the presence of mercaptoacetic acid. After adjusting the pH of the purified beryllium solution to 11.5 and

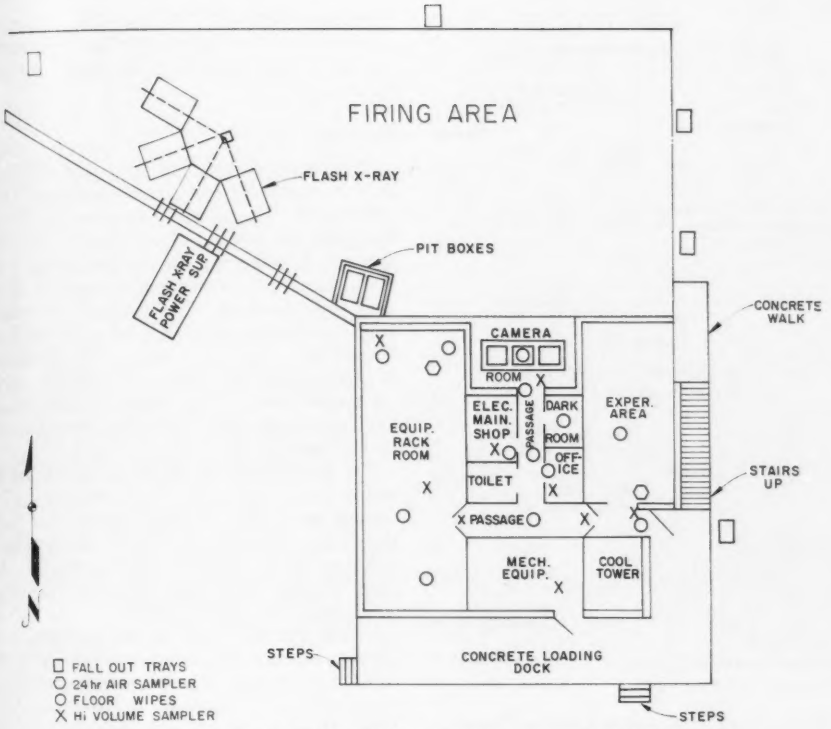

FIGURE 2. Plan view of Bunker 302 showing relative sample sites for survey.

the sodium perchlorate salt concentration to 1*N*, the reagent morin (pentahydroxyflavone) is added to the sample. The fluorescence of the beryllium-morin compound thus formed is measured and compared to standards.

Results

Figure 2 is a plan view of the bunker interior and exterior. The approximate locations where samples were taken during this study, which was conducted in 1959 and 1960, are indicated. Presented in Tables I through IV are the results of samples taken during various phases of activity in the bunker environment and surrounding area.

All but 11 of 56 air samples taken in Bunker 302 measured less than 0.01 μg of beryllium per cubic meter of air. Results of the eleven measurable samples are illustrated in Table I. Sixty air samples were taken outside Bunkers 302 and 312. Samples were taken in the breathing zone of personnel while they were engaged in routine activities. Forty-five of the sample results measured less than 0.1 $\mu g/m^3$. Those activities which demonstrated higher results are shown in Table II.

Historical (24-hour) air samples were taken at distances of 2600 feet north by northwest, 4200 feet west, 4800 feet southeast, and 8.4 miles to the northeast of Bunker 302. A total of 749 samples were taken and all results were zero.

Soil samples were taken at the test site and control samples were taken at various locations in the Livermore Valley area. The Valley area was divided into three zones. The zones are, respectively, 0 to 2 miles; 2 to 5 miles; and 5 to 10 miles from the Laboratory. The average of 36 samples in zones 1 and 2 was 0.5 $\mu g/g$ of soil. The average of 36 samples in the third zone was 1 $\mu g/g$ of soil. These samples reflect the 325-mesh fractions of soil samples. At Bunkers 301, 302, and 312, soil samples were taken at ground zero and radially outward to distances of 1000 feet. The results of the 325-mesh fractions are illustrated in Figure 3.

Several soil samples collected at the test site were sieved into three fractions: less than 44 microns; 44 through 149 microns; and larger

TABLE I

Air Samples inside Bunker 302

Station	Beryllium Concentration ($\mu g/m^3$)			No. of Samples
	Maximum	Minimum	Average	
Inside bunker door (during shot)	0.14	0.02	0.08	5
Inside bunker door (after shot)	0.05	0.01	0.03	3
Inside main door	—	—	0.14	1
Control room	—	—	0.07	1
Office	—	—	0.04	1

TABLE II

Breathing Zone Air Samples Outside Bunkers 302 and 312

Work Activity or Location	Beryllium Concentration ($\mu g/m^3$)			No. of Samples
	Maximum	Minimum	Average	
Cable manipulation	—	—	0.27	1
Loading debris into truck	—	—	0.44	1
Raking and stacking debris	0.95	0.1	0.30	7
Grading and leveling gravel	—	—	0.15	1
Cleaning hose pit box	—	—	2.40	1
Outside bunker door	0.28	0.1	0.19	3
Outside apron during shot	—	—	0.11	1

than 149 microns in diameter. A typical distribution of the fractions is illustrated in Table III.

In Bunker 302, 145 wipe samples were taken. Of all samples taken, four were greater than 0.01 $\mu g/cm^2$. The average of these four positive samples was 3.5 $\mu g/cm^2$. The tops and bottoms of several pairs of shoes were wiped. The highest value obtained from these samples was 1.6 $\mu g/cm^2$.

At the test site there are six wells which provide water for the project. Three wells are located in the immediate firing area and the remainder outside this area. From these six wells 202 samples were taken. Of these, six were greater than 1 μg/liter. The maximum reading obtained was 2.5 μg/liter, and in this instance sample contamination was suspected. Upon resampling, this was substantiated. Tap water from the Laboratory in Livermore was assayed for beryllium and all sample results were zero.

Table IV illustrates the results obtained from washing coveralls and socks of personnel following work on the firing table. Serving as controls were clean coveralls and socks not worn on the table. Thirteen respirator cartridges were analyzed for beryllium. Ten of these cartridges had less than 0.2 μg/cartridge, and the remaining cartridges were 0.8, 2.0, and 2.8 μg/cartridge, respectively. Respirator cartridges not worn on the table were assayed for beryllium. All results were zero.

Discussion

The presented data indicates that the interior of the bunker is free from contamination, as anticipated. This is best explained by the construction, the method of ventilation, and the effort put into keeping the interior of the bunker clean. Bunker housekeeping is required to meet very high standards. For instance, the following tasks are routinely accomplished as indicated: floors are vacuumed daily; the Mechanical Equipment Room is vacuumed weekly; and the air-conditioning ducts, light fixtures, tops of electronic racks, pipes, etc., are cleaned monthly by vacuuming.

The build-up of beryllium on the firing table and surrounding area was surprisingly low. This finding seems best explained by several factors. Beryllium, being a light metal, when subjected to these detonations is either vaporized or oxidized to some extent and widely dispersed by the wind and air currents. Results of the soil samples indicate that most of the material is confined to within a couple hundred feet of the firing table. This finding resulted in establishing arbitrary operational limits for beryllium in the soil. When these limits are exceeded the area is decontaminated. This is usually accomplished by the removal of soil, covering with a layer of uncontaminated soil, and/or spraying with water or oil. The limits are as follows:

1. *500 μg/gram of soil* in areas where beryllium operations are in progress provided that the average air-borne concentration in the area does not exceed 2.0 $\mu g/m^3$, and the short-term (30 minute) concentration does not exceed 25 $\mu g/m^3$.

2. *100 μg/gram* for on-site areas where beryllium operations are not in progress, provided that the average air concentrations in the area do not exceed 0.2 $\mu g/m^3$, and short-term concentrations do not exceed 25 $\mu g/m^3$.

In addition, craters made by detonations are back-filled with fresh gravel; thus a continual dilution of the firing table contamination occurs.

A potential air-borne risk occurs when firing table material is moved or disturbed. Data on protective clothing indicate that beryllium could be transported to other on-site areas or to the home environment if controls were not exercised. On the basis of these results the following personal hygiene and safety practices were established to safeguard the health and welfare of per-

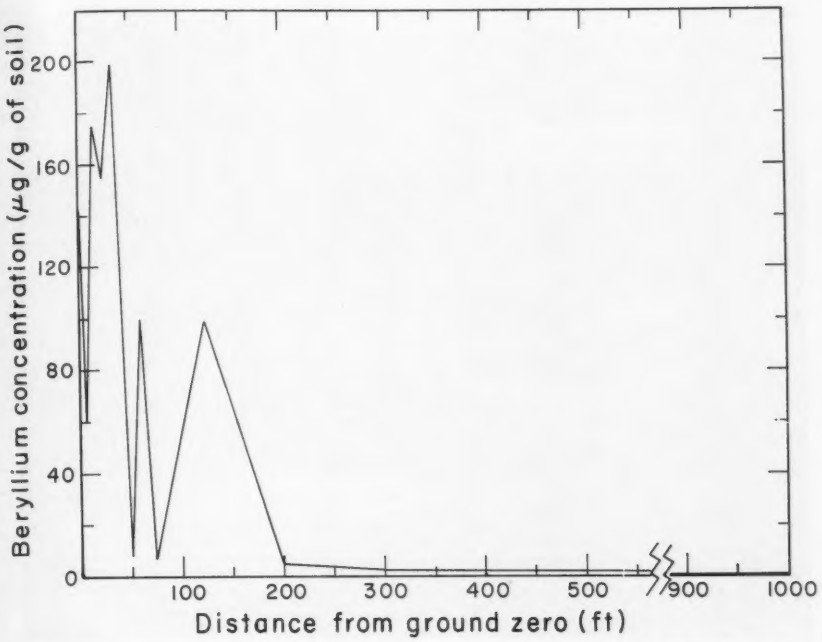

FIGURE 3. Average concentration relationship for 325-mesh fractions of beryllium from bunker tables.

TABLE III

Soil Samples Expressed as % by Weight

Location	Beryllium Fractions		
	<44 Microns	44 to 149 Microns	>149 Microns
301 Table	2.5%	14.7%	82.8%
312 Table	5.8%	7.3%	86.9%
Road Dust	4.1%	8.9%	87.0%
Northwest Area of Site	12.6%	35.5%	51.9%

sonnel who work in or frequent the test site area. These are summarized as follows:

A. Industrial Hygiene Practices

1. For personnel who work on or frequent the firing table, protective clothing is required. If the gravel on the table is to be moved, a half-mask respirator with a high efficiency filter is provided. Protective clothing, changed on a daily basis, includes laboratory-provided coveralls, shoes, socks, and caps. Visitors to the table are allowed during periods when no gravel or table material is being disturbed. Shoe protection, in the form of "bootees", is provided for visitors.

TABLE IV

Beryllium Found in Coveralls and Socks after Use on Firing Table

Time Worn on Table (hours)	Beryllium Concentration (μg/coverall)		No. of Coveralls per (μg/coverall) Range			Total No. of Coveralls
	Maximum	Minimum	<37	37 to 112	>112	
0 (Control)	28	<19	18			18
1	<19*		1			1
2	<19	<19	3			3
3	<19*		1			1
4	112	<19	1		1	2
6	<19*		1			1
8	<19*		1			1
10	37	<19	3	1		4
23	159*				1	1
40	47	<19	1	1		2
Socks (4 pairs)	178	<19	2		2	4

* Single value recorded as maximum value

2. A ten-minute waiting period is mandatory before personnel are allowed on the firing table after the detonation of a high explosive test assembly. This period, while the personnel are waiting in the bunker, permits the cloud made

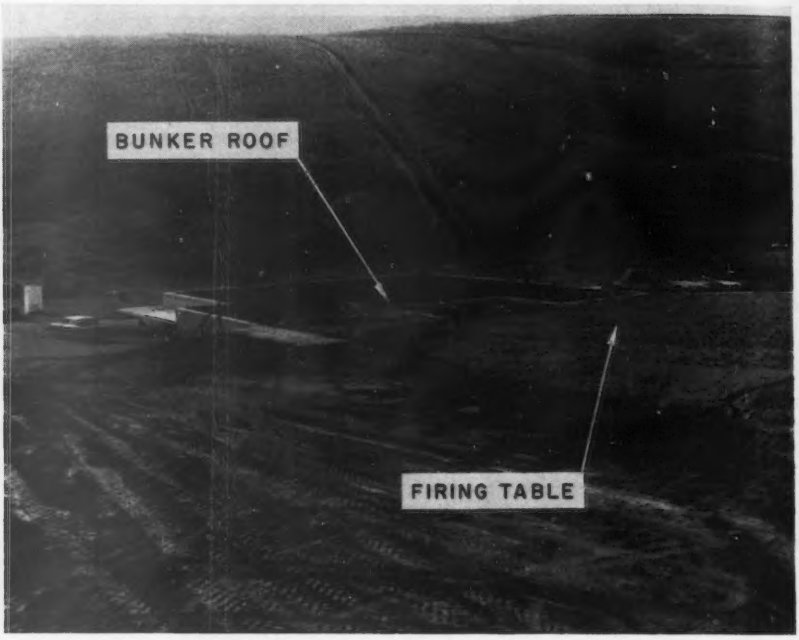

FIGURE 4. General view of site showing relative locations of Bunker 302 roof and firing table.

by the test-fired assembly to dissipate to such an extent that virtually no air-borne contaminants remain.

3. The interior and exterior of the bunkers are cleaned on a routine basis. Vacuuming of floors and walls rather than sweeping, for example, typifies the techniques employed. Exterior bunker walls, docks, and stairs are routinely washed down with water. Vehicles used to transport personnel and equipment are cleaned by vacuuming the interior and washing the exterior.

Personnel who work only inside the bunker are not required to follow the above practices. Inside, the bunker is considered a "clean" area. Therefore, those personnel need not wear protective clothing.

The top of each bunker, illustrated in Figure 4, is covered with loose gravel to a depth of approximately 16 feet. Gravel serves as a shock absorber for hydrodynamic test assemblies. Prior to and after the test firing of each hydrodynamic assembly the table is sprayed with water. After each test firing the crater made by the test assembly is back-filled with fresh gravel. Water tends to keep the dust from rising, and back-filling reduces the build-up of beryllium concentrations at the point of firing.

B. Change Room and Eating Area

At present, personnel change their clothing at a centrally located facility. All personnel are required to pass through this facility prior to going to the firing area. At the entrance to each bunker a sink is provided for personnel to wash their hands. Eating areas inside each bunker are provided.

C. Surface Contamination

The interior of each bunker is clean. In order to preserve this concept, high standards of cleanliness are required. With this in mind it was necessary to establish arbitrary operational standards for beryllium contamination within the bunker interior and for other equipment used at the test facility. The standards for surface contamination are as follows:

floors and walls	0.02 $\mu g/cm^2$
unenclosed equipment	0.01 $\mu g/cm^2$.

Should these values be exceeded, the contami-

nated area would be thoroughly cleaned. This is accomplished by the use of soap and water or by vacuuming.

Summary

A study was made of beryllium exposures at a high explosive assembly test facility. Beryllium metal, included in high explosive assemblies when detonated, is vaporized, oxidized, and widely dispersed by wind and air currents, and that which remains is confined within a few hundred feet of the firing table. Results of the investigation indicate that the disturbing or moving of firing table material, such as by digging or raking, demonstrated the most significant findings. The industrial hygiene practices that are employed at the test facility are described. These practices are necessary to safeguard the health and welfare of personnel who are associated with this type of facility.

Acknowledgments

The helpful suggestions of Max W. Biggs, M.D., Ross Kusian, William Morris, Walter Boyle, and many others who offered their assistance, are hereby acknowledged with thanks. Work was performed under auspices of the U. S. Atomic Energy Commission.

References

1. *STATUS, Fiscal Year 1958*, Lawrence Radiation Laboratory, University of California, Berkeley and Livermore.
2. SILL, C. W., AND C. P. WILLIS: The fluorometric determination of submicrogram quantities of beryllium. *Anal. Chem. 31:* 598 (1959).

NEW RESEARCH CENTER

THE KOPPERS COMPANY, INC. on August 28, 1961, dedicated a new, large research facility at Somervell Park, Monroeville, Pennsylvania. It represents an investment of approximately eight and one-half million dollars although only about one-third of the buildings planned for the 176 acre site have been completed. No firm schedule for construction of the remaining buildings has been set, however the Center will eventually be able to house over 1500 scientists and their assistants, about four times its present population. The Center itself consists of a 5-story administration building, three 3-story interconnecting laboratory wings and several outlying auxiliary buildings. A feature of the Center which contributes to its easy expansibility are the glass enclosed stairways at the end of each wing for easy removal when additions are to be made. Besides this new Center, Koppers operates eight other research and development facilities of varying sizes where product and process control, application research, and pilot plant operations are the principal activities.

Until relatively recently, Koppers Company, Inc. had been largely identified with engineering and construction, mostly in the steel industry, coal by-products, wood preserving, fabricated metal products, and merchant coke plants. Now they have moved into the fields of chemicals and plastics with a vigorous research program for new product development. At the dedication of the new Center Mr. Fred C. Foy, Chairman of the Board, mentioned some of the current research projects in boron chemistry, plastics for building materials, fiber reactive dyes, chemical intermediates, a dye for anodized aluminum, and a process for the desalinization of sea water.

Making Known Concentrations for Instrument Calibration

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The use of prepared gas samples of known concentrations is imperative for the calibration and verification of the performance of many industrial hygiene and safety instruments. Batch (static) and continuous mixing (dynamic) techniques for preparing and using known mixtures are described with discussion of advantages and limitations. The use of commercial field test kits and compressed gas cylinders is widely accepted.

Introduction

THE need to know whether a work place is safe for workers has prompted over the years the development of innumerable instruments and other devices to monitor industrial atmospheres for toxic and explosive concentrations of gases and vapors. The industrial hygienist who trusts one of these devices to make such a determination where the health and safety of workers is involved will sooner or later wish to verify for himself that the answer which is given him is the right answer. The simplest and quickest method of performing such an integrity test is to sample from a source of contaminant of known concentration.

The method by which mixtures of gases and vapors are made for this purpose, and the certainty with which they are labeled "known" is of concern equally to the person who will use the mixture to check his monitoring devices, and to the manufacturer who has provided him with these devices. It is the purpose of this paper to outline in useful detail several of these methods which have enjoyed rather widespread acceptance, and to discuss necessary precautions and possible pitfalls sufficiently that the user may obtain meaningful and reliable results from his efforts. It is hoped that with adequate awareness of the ease with which proper calibrations may be performed, there will be a corresponding decrease in the use of practices which are of questionable value and which further may have a damaging effect on the elements of instruments involved.

There are many procedures which have been employed from time to time and for more or less special applications which will not be covered in detail. Many of these have been published, and where the method appears to be of sufficient interest, a reference will be found. Recently one writer, Gilliland[1] has summarized a number of methods but not in sufficient detail to be useful in setting up and operating any of the methods discussed. The methods discussed in the following, while primarily of interest in calibration of devices for detection of toxic and explosive hazards are equally applicable to other calibration problems, and have seen much use in calibration of process stream analyzers of many types.

In toxic and explosive hazard work, the concentration of the contaminant which is of interest can vary over a very wide range. As an example, the Threshold Limit Value for arsine is 50 parts per billion, while that for ethanol is 1000 parts per million, which is 20,000 times greater. A good source of this information is the yearly publication of *Threshold Limit Values* by the American Conference of Governmental Industrial Hygienists.

Explosive limit values are at a much higher level, and the interest is generally in the lower explosive limit, or LEL. Typical values are 1% for octane, 4.0% for hydrogen, 5.3% for methane, and 12.5% for carbon monoxide. A good source of this information is *Bulletin Number 503* of the U. S. Bureau of Mines (1952), or in *Fire-Hazard Properties of Certain Fammable Liquids, Gases and Volatile Solids* National Fire Protection Association Booklet No. 325 (1960).

The predictable mixing of gases and vapors is made possible by the gas laws (Boyle, Charles, Dalton, and Avogadro) which are familiar to most of us. At atmospheric pressure, most gases and vapors behave essentially as ideal gases. However, at pressures higher than atmospheric

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most depart from ideality, some more rapidly than others, and serious errors can result if appropriate corrections are not employed. For most of the procedures to be described here, ideality corrections are unnecessary. Compressibility data is readily available, however, and corrections can be made using these if desired.

The easiest and most used classification of methods of preparing known mixes for calibration purposes is batch and continuous. The first of these prepares a definite, generally small volume and is used where smaller quantities will suffice. Where larger volumes are needed, a continuous stream is prepared. A simple, easy to follow procedure for a basic mixture by either method will be described, followed by various useful modifications of details in order to cope with special requirements.

Batch Methods

Fixed Volume

The choice of container in which to prepare a batch sample will depend on the size of the sample needed and the nature of the gases or vapors from which the sample is to be prepared, assuming that a rigid container is selected. Glass is a convenient material and is frequently used because of its ready availability and general inertness. Materials which are reactive to or adsorptive to the constituents of the mixture are unsuitable. Volume of the container should be at least four times the volume of the sample which will be required to be drawn from it.

Figure 1 illustrates a typical assembly for which a 5-gallon glass bottle has been selected as the container. Three connections are shown through the stopper which seals the bottle neck. One short connection to the top is used for filling, the other for sampling. The third or long connection which extends to the bottom is used to admit makeup air during use to maintain atmospheric pressure in the bottle. If makeup air is admitted at the top through one of the short tubes, at high withdrawal rates the makeup air will stream in so rapidly that mixing with occur from top to bottom and the concentration will fall rapidly. At low flows—a fraction of a liter per minute—however, it is often preferable to withdraw from the bottom and make up at the top because mixing danger is minimized by the low flow and dilution of the sample by stopper leakage is less likely.

The volume of gas or volatile liquid required to produce a given concentration in a container of known volume may be calculated by the following equations. These equations assume pure gas or liquid. Use of gas or liquid less than 100% will require that the calculated volumes be increased proportionally.

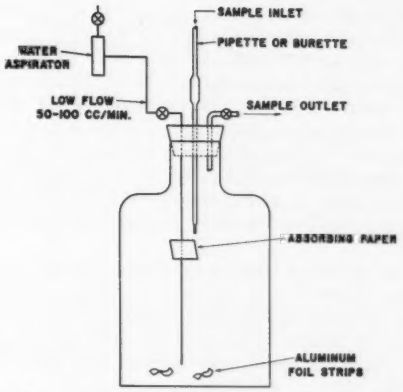

FIGURE 1. Use of 5-gallon mixing bottle.

A. Mixtures in Percentage Composition

$$V_G = C_1 \times 0.01 \times V_H \tag{1}$$

$$V_L = \frac{C_1 \times 0.01 \times V_H \times MW_L \times 273.1 \times P}{d_L \times 22{,}400 \times 760 \times T} \tag{2}$$

B. Mixtures in Parts Per Million Composition

$$V_G = C_2 \times V_H \times 10^{-6} \tag{3}$$

$$V_L = \frac{C_2 \times V_H \times MW_L \times 273.1 \times P}{d_L \times 22{,}400 \times 760 \times T \times 10^6} \tag{4}$$

where

- V_G is required volume of contaminant gas in ml,
- V_L is required volume of contaminant liquid in ml at temperature T,
- C_1 is desired final contaminant concentration in per cent,
- C_2 is desired final contaminant concentration in ppm,
- V_H is volume of housing or container in ml,
- MW_L is molecular weight of contaminant liquid,
- P is barometric pressure in mm Hg,
- d_L is density of contaminant liquid in gm per ml at temperature T, and
- T is temperature of apparatus °K.

The calculated volume of contaminant gas or volatile liquid required may be added by glass syringe, burette, pipette, or ampoule. During addition of gases to a container, a slight suction should be maintained on the container (as with the water aspirator) so that all of the gass added

will be drawn into the main body of the mixture.

For low concentrations, the liquid is allowed to drip onto a piece of suspended filter paper rather than fall into the bottom of the container. To insure mixing of the vaporized liquid, strips of aluminum foil are included which may tumble through the gas and promote mixing as the bottle is repeatedly inverted. Samples in larger containers such as drums and carboys may be mixed with a small motor-driven fan through a mercury seal.

As a general rule for containers having a volume of one to five gallons, about one-fourth of the gas mixture may be withdrawn before diffusion or mixing of makeup air into the sample causes a noticeable reduction in gas concentration.

Stead and Taylor[2] have attacked this problem somewhat differently by attempting to insure perfect mixing and by using the calculated diluted concentration value as samples are sequentially withdrawn.

Setterlind[3] has used several bottles, all filled with the same mixture, in series, and has demonstrated that for a fivefold increase in sample volume mixed, a thirtyfold increase is made in usable sample thereby.

Variable Volume

Another approach to avoiding dilution and thus making more of the mixed sample available for use is the substitution of a non-rigid container, such as a flexible bag of plastic or metal foil, or a gas holder for the bottle or drum described previously. With these devices a reduction in contained volume occurs as the sample is withdrawn and concentration remains fixed. Use of the flexible bag can also remove the size limitations which often attach to rigid containers. Extruded or fabricated bags can be obtained or made to quite large volumes at insignificant cost. This method cannot be used if one of the gases or vapors in the mixture can dissolve in, diffuse through or adsorb on the walls of the container, or can be absorbed in the liquid in the seal of the gas holder. These are important limitations and definite knowledge of them should be secured prior to experiments. A limited amount of wall adsorption is probably always present, and if concentrations being dealt with are so low that results are vitiated in this manner, a prior mix and flush will generally result in conditioned walls.

In filling containers of variable and thus uncertain volume, the air or gas is metered in and the fill is stopped before the container is completely full to avoid back pressure. The minor constituent is bled in about midway of the filling cycle.

The metal gas holder with liquid seal and removable top bell has been found convenient in preparation of samples requiring more or less large volumes of volatile liquids because it permits easy internal installation of heaters for vaporization and fans for mixing of the sample prior to use.

Under certain circumstances mixture of gases or vapors in the explosive range may be desired, as when testing flash-back arrestors. In such cases, the volume of explosive mixture should be kept small (just large enough for the test), the container should have a blowout panel, and the apparatus should be surrounded by shields to protect personnel. Use of a gas holder with a water seal will limit these mixtures to atmospheric pressure, and if a sheet of cellophane is used as a cover on the top of an open bell, protection against damage by explosion will be maintained. Use of such a setup has proven successful with hydrogen-oxygen mixtures, but is still hazardous with mixtures of acetylene and oxygen.

A typical procedure for filling and using a flexible bag follows:

(1) Deflate the bag to as near zero volume as possible.
(2) Meter air into the bag until it is slightly less than formed.
(3) Bleed a measured volume of contaminant by means of a suitable gas burette into the metered air entering the bag during the middle of the filling operation.
(4) Mix by pressing on various parts of the bag and/or having loose strips of metal or plastic foil in the bag as it is turned end for end or revolved.

Pressure Cylinders

A modification of the batch technique which can furnish larger quantities and at elevated pressure is the preparation of a mixture of the desired composition in a gas cylinder.

Such mixtures may be prepared at pressures of 10 atmospheres in Air Force oxygen cylinders or at higher pressures in appropriate gas cylinders. The method for low pressure cylinders has been described recently by Baker and Zinn[4] and the method may be extended to cover high pressure cylinders. Cylinders are first evacuated, then filled in steps using accurate gauges and pure gases so that the partial pressure of each gas (the difference between initial and final cylinder pressures as the gas is added) is equal to the product of the mole fraction of the gas in the mixture and

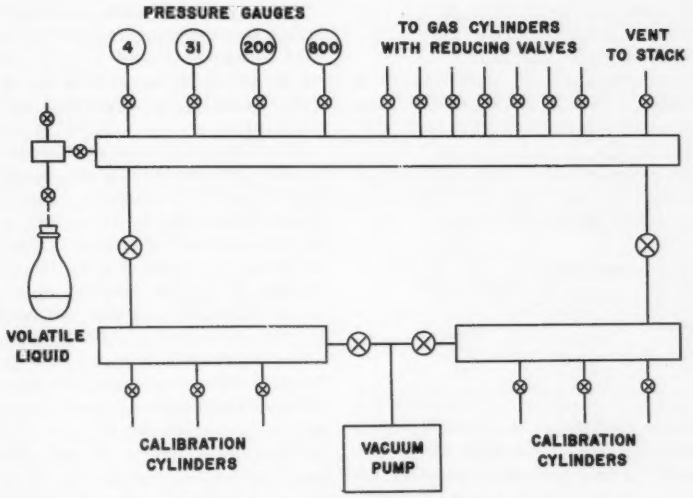

FIGURE 2. Low pressure cylinder filling device.

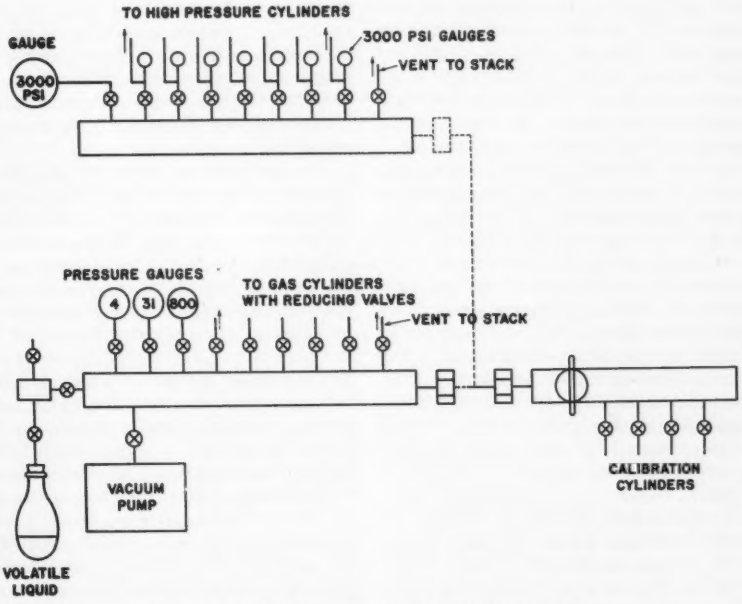

FIGURE 3. High pressure cylinder filling device.

the final absolute cylinder pressure. Cylinders may be filled on the equipment illustrated schematically in Figures 2 (low pressure) and 3 (high pressure).

By using the low pressure apparatus with accurate gauges and filling the cylinders slowly over a period of thirty minutes so that heat generated by compression of the gas may be dissipated, gas mixtures accurate to 1% of the gas concentration may be prepared.

Compressibility of non-ideal gas becomes a problem at either low or high pressures by this

method, and corrections must be made if a verifying analysis is not to be made. This is adequately covered by Baker and Zinn.[4]

High pressure cylinders are more difficult to prepare in a short period of time because the mass of gas and cylinder is greater and the heat effect is greater due to the compression to a higher pressure. Such cylinders filled, then analyzed for gas composition, have shown the following deviation from the desired gas concentration:

Total Percentage of Cylinders Filled	Deviation from Desired Gas Concentration
40%	None
60%	±2%
80%	±5%

Preparation of mixtures of low concentrations in the 0–1000 ppm range are best made by two mixes. A cylinder is first prepared containing 1% of the desired gas, then this mixture is diluted to obtain the low gas concentration.

Since the preparation of high pressure gas cylinders might be difficult and dangerous for many laboratories, such mixtures may be purchased from several sources. These cylinders are satisfactory sources of calibration gases such as carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, etc., and may be purchased at a pressure of about 1500 psi. Cylinders containing vapors of volatile liquids or of gas concentrations such that the partial pressure of the gas in the cylinder is near the vapor pressure of the gas at the lowest temperature to which the cylinder will be exposed require care in storage and use. The pressure to which such a cylinder may be filled may be much lower than 1500 psi. The cylinder pressure which may be used is determined by the ratio of the saturated vapor pressure of the vapor at the lowest anticipated temperature of storage and use and the mole fraction of the vapor in the cylinder. For example, a cylinder to contain 1% by volume of acetone in air for use at 5°C could be filled to a pressure of 1.72 ÷ 0.01 or 172 psia (since the vapor pressure of acetone at 5°C is 89 mm Hg or 1.72 psi). This is equivalent to 181 psia or 166 psig at 70°F.

Storage of this cylinder at a temperature below 5°C would result in condensation of liquid acetone and a change in the gas concentration. Before such a cylinder may be used with accurate results, the cylinder must be warmed and mixed to reconstitute the gas mixture.

High pressure cylinders of ordinary gases may be used with reducing valves for calibration purposes. However, some gases, hexane, benzene, etc., will be absorbed in the diaphragms of some reducing valves and any rubber tubing used. Such mixtures should be used through needle valves and metal connectors, taking care that the flow system is open to prevent buildup of unsafe pressures.

A number of general precautions may be mentioned. For obvious reasons, mixtures within or approaching the explosive range should not be made. When oxygen (or air) is to be part of a mixture, the mixing procedure should be planned so as never to pass through the explosive range during the mixing process. This is most often accomplished by diluting the combustible with nitrogen prior to adding oxygen.

Certain substances with relatively high positive heats of formation (acetylene can be used as a typical example) can detonate when the pressure is raised, even in the absence of a combustible mixture or of oxygen. In the case of acetylene, manifold partial pressures in excess of one atmosphere absolute are not permitted. The acceptable pressure varies from compound to compound, and hazardous materials should not be used unless definite knowledge of any necessary precaution is available. Many people limit materials from which manifolds and connections may be fabricated to non-copper bearing alloys because of the danger of formation of copper acetylid.

The stability of mixtures prepared in high pressure cylinders may be good or it may be bad, and this depends on several factors including material from which the cylinder is constructed, its cleanliness, the nature of the gas mixture, and the peculiarities of the individual constituents. A calibration cylinder of carbon monoxide in air prepared at the National Bureau of Standards has maintained a constant concentration for a period now in excess of 5 years. A cylinder containing a small concentration of hexane in nitrogen has exhibited stability in excess of two years. On the other hand, a cylinder with ½% HCN in nitrogen has been losing concentration at the rate of 15–20% per year for three years, primarily because of a polymerization reaction with HCN.

Cylinders containing nickel carbonyl in nitrogen lose their $Ni(CO)_4$ content completely in a very short period of time. Similar concentrations with carbon monoxide substituted for nitrogen also disappear if the original $Ni(CO)_4$ is not above 100 ppm. However, a 350 ppm concentration reduces in a period of about a month to 250 ppm then remains stable at this level. This is because of the ready decomposition of $Ni(CO)_4$ in the presence of traces of oxygen and water vapor. The mass effect of CO on the equilibrium of the

reaction has a stabilizing influence even though residual oxygen and water vapor effects are still present.

In general, mixtures in which the gas of interest is at a low ppm level may be expected to decrease in concentration level over a long period of time. Wall adsorption in a large cylinder probably accounts for a considerable proportion of the loss which is experienced, but reaction, decomposition, and polymerization are important contributors also.

It is hoped that the complexity of the apparatus and the precautions which have been cited will discourage all but the most careful investigators from attempting this high pressure mixing. If use of such an apparatus appears advantageous to you, be sure your equipment is adequate and clean, that proper safeguards exist for both operating and surrounding personnel, and that you have a thorough knowledge of all the materials you wish to handle. Failing this, buy your high pressure mixtures from one of the commercial sources.

Field Kits

A good example of the batch mixture method, engineered for simplicity of use in the field is the J-W Gas Indicator Test Kit (Figure 4) which is composed of a soft plastic bottle (350 cc) with a special cap and 24 glass ampoules filled with methane. All are packed in a white cardboard box container measuring 7¼" x 4⅝" x 2⅜".

Each sealed ampoule is filled with a measured volume of combustible gas. The ampoule is broken in the plastic bottle by vigorously shaking the closed container until the ampoule is shattered by the metal "breaker". When the ampoule is broken, a specific methane-air mixture is formed.

The gas-air mixture is then forced from the soft plastic bottle by squeezing it as desired into the inlet of the instrument being checked. It is important that the grip not be relaxed or air will be drawn in and dilute the sample. The plastic container is flushed several times with air before reuse.

Another device which performs a similar field test function is the MSA Field Calibrator. As illustrated in Figure 5, it consists of a metal gas holder capable of producing approximately 600 ml of gas-air mixture, a pressure container for holding and dispensing combustible gas, a calibrated syringe for measuring the combustible gas volume and transferring it to the gas holder, and small cartridges of compressed gas (isobutane). The gas holder is a cylinder and piston assembly.

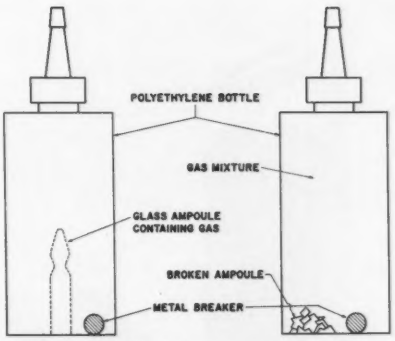

FIGURE 4. J-W Gas Indicator Test Kit.

The calibrator is operated as follows: a cartridge of compressed gas similar to those used in desk-type cigarette lighters, holding enough gas for approximately 100 tests is placed into the pressure container and as the cap is closed, the cartridge is punctured, allowing the gas to escape into the container, where it is confined by means of a pressure type release valve. The air in the gas holder is expelled by seating the piston as far as possible. The calibrated syringe is then completely filled with gas by momentary contact with the pressure release valve on the gas container.

The desired volume of gas is measured by expelling the excess gas from the syringe by means of the piston, and the syringe is then attached to the gas holder. As the piston is raised, the gas in the syringe is drawn into the holder. When suction is created as the syringe piston seats, a small valve in the plunger opens, admitting air to the gas holder to complete the sample volume and produce mixing. The syringe is then disconnected from the gas holder and the combustible gas indicator sampling line is attached by means of the adapter, which opens a check valve in the connection to the holder so that the gas mixture can be withdrawn.

For field use, both the J-W and the MSA devices are extremely convenient. They are small, lightweight, readily carried about, and require no external accessories in order to set up and make tests on instruments.

Continuous Flow Methods

Basic Mixing System

The basic requirements for a continuous gas mixing system are very simple; two streams of accurately metered gas and a mixing chamber. This typically simple system is illustrated in Figure 6. Metering is accomplished by control of

FIGURE 5. MSA Field Calibrator.

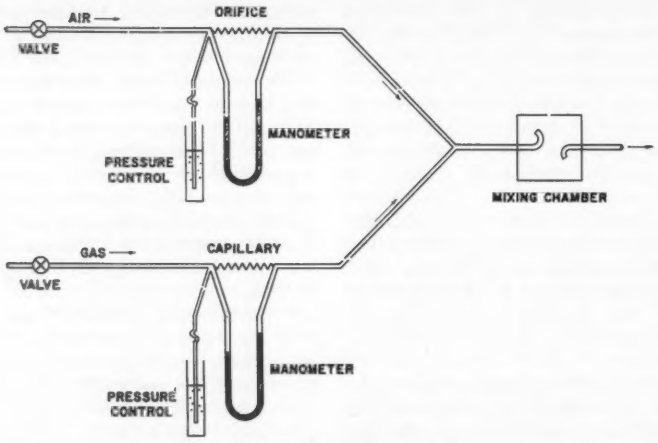

FIGURE 6. Continuous gas mixer.

the pressure drop across calibrated orifices or capillaries in the individual lines. Calibration establishes the relation between volume flow through the orifice or capillary and pressure drop across it, and the manometers illustrated allow ready monitoring of adjustments to verify the mixture being made. A needle valve between the pressured source of gas or air and the orifice, and an overflow tube to permit easy adjustment of pressure and venting of surges make the system easy to keep at a constant output. Adjustment is accomplished by fixing the hydrostatic head

against which overflow is possible, and regulating the needle valve to a slow steady bubbling from this overflow. Such a system should vent to the atmosphere to avoid problems with back pressure. It is convenient to construct such systems of glass and with ground tapered or ball joints, assembly and disassembly is not difficult. Alternatively, metals and other materials with plastic and rubber tubing for connections may be used, but only if it is known that adsorption and diffusion do not occur and vitiate the results.

Selection of orifices and capillaries to provide proper flows at convenient pressure differentials is desirable. Orifices may be drilled plates, or short lengths of larger bore capillary or heavy wall glass tubing, and can accommodate flows from several hundred to several thousand ml per minute. Capillaries which are readily available in glass from laboratory supply houses are useful for flows down to a limit of about one ml per minute. Below this, they are difficult to obtain, and moreover, plug too readily to be useful in such an apparatus. Operating pressure differentials should be selected in a range above 50 mm H_2O to as high as 250 to 300 so that significant adjustment can be made, and so that the minimum observable manometer fluctuation, which is generally about a millimeter, does not constitute a significant change in operating conditions.

Adherence to these principles generally does not permit a sufficent range of operating conditions to arrive at contaminant concentrations in the low ppm range without excessive air flows. This may be overcome by using a first mixture as described above as the feed contaminant to one orifice of the second stage of a two stage mixture, where it is again diluted with another air stream to the desired level. Such an apparatus is generally referred to as a Double Dilution Apparatus. The considerations involved in such a setup are identical to those already covered with the exception that the first stage must operate at a sufficiently high back pressure to feed the second stage.

Calculations involve simple ratios of volume flows:

$$C_1 = C_0 \frac{V_1}{V_1 + V_{A1}} \tag{5}$$

$$C_2 = C_1 \frac{V_2}{V_2 + V_{A2}} \tag{6}$$

where

C_0 is purity of inlet contaminant stream, consistent units;
C_1 is effluent contaminant concentration from first stage, consistent units;
C_2 is effluent contaminant concentration from second stage, consistent units;
V_1 is contaminant stream flow, first stage, consistent units;
V_2 is contaminant stream flow, second stage, consistent units;
V_{A1} is air stream flow, first stage, consistent units; and
V_{A2} is air stream flow, second stage, consistent units.

One or two additional words of caution are helpful to those using this method:

(1) Allow adequate time for equilibrium to be established when starting up. Lines to and from capillaries metering a few ml of gas per minute do not flush rapidly. This problem can be minimized during the design and assembly period by avoiding dead volumes and long lines.
(2) Clogging of orifices and capillaries with dirt, dust, or products of decomposition of the gas being metered can vitiate calibrations over the course of time. Analysis of the effluent or a periodic recheck of calibrations can avoid this type of difficulty.
(3) Loss of gas by absorption or reaction with manometer liquids is possible if liquid selection is not carefully made.

A very useful modification of the basic pressure control system described above where variation of back pressure is likely to occur is the scheme described by Oberfell and Mase[5] in 1919, and later patented by Mase[6] in 1924. The details of this scheme are shown in Figure 7. The basic flow pattern is identical to that of Figure 6 as described above. Its difference resides in the treatment of the pressure control portion. A pressure compensating connection is made from the effluent side of the flowmeters to the trapped gas space above the liquid in the large bottle to the left, labeled A. Tubes B and C serve a similar function to the pressure control tubes of Figure 6. Adjustment of the depth of the center bubbler tube regulates the hydrostatic head against which overflow of excess gas occurs, and thus fixes the differential pressure across its respective capillary or orifice. If the mixing bottle exhausts to atmosphere, the level of liquid in the tubes B and C will coincide with that in the bottle at A. If, however, the mixing bottle exhausts to a pressure higher than atmospheric, this back pressure will be communicated via the pressure compensating tube to the closed space A above the liquid in the bottle. This increased pressure will in turn cause a rise in the liquid in tubes B and C above that at A, thus raising the hydrostatic head

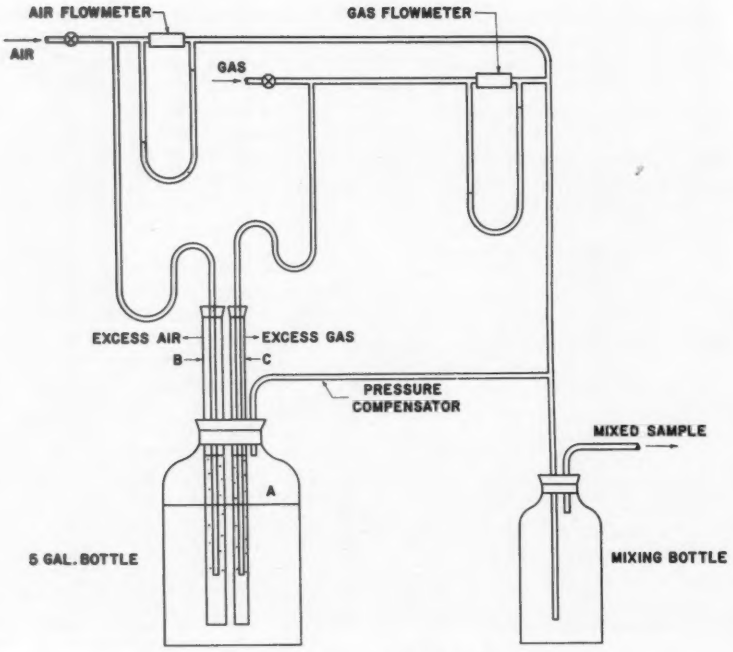

FIGURE 7. Modified Mase mixer for calibration gas.

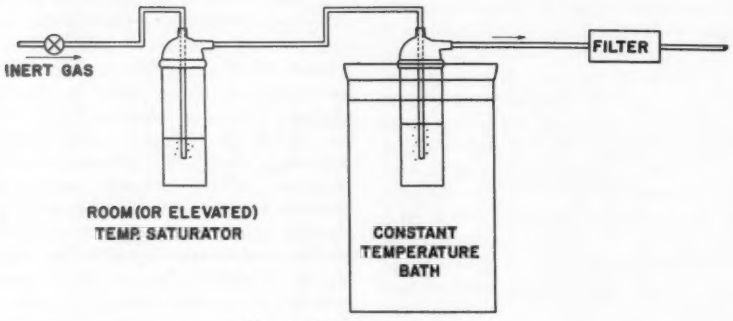

FIGURE 8. Vapor saturator.

against which excess gas can escape. The net result is an almost constant differential across the orifices or capillaries, and hence, an almost constant flow.

It is obvious that the pressure compensation afforded by this apparatus is not absolute since a rise of level in tubes B and C is accompanied by a fall of level in bottle A. This fall is in proportion to the relative cross sections of tubes B and C and bottle A. The cross section of the bottles should be at least 50 times and preferably 100 times the cross section of the tubes B and C.

Up to now concern has been with continuous mixing of two gas streams. If one of the constituents is to be the vapor of a volatile liquid, then there are several useful methods available which can be substituted for the metered flow of gas which has been discussed.

Pure Liquids

For pure liquids, the saturation method illustrated in Figure 8 is convenient. Depending upon

the vapor pressure of the liquid to be vaporized, the first saturator may be maintained at room temperature, or at a slightly elevated temperature, and its effluent passed to a second saturator which is maintained at a somewhat reduced temperature in a constant temperature bath. The temperature of melting ice is often the most convenient level for this second saturator.

A flow of inert gas appropriate to the analysis involved is bubbled through the two saturators in series, picking up the vapor of the liquid to be volatilized. Saturation in a single saturator is seldom complete, often running as low as 50%, and infrequently higher than 90%. If the stream from the first saturator is passed to the second at a fixed and lower temperature, condensation should take place, and it should then be safe to assume 100% saturation at the fixed temperature of the second saturator, and Dalton's law of partial pressure should give an accurate value for concentration in this stream. With liquids (such as hydrogen fluoride) which tend to produce mists or fogs when so treated, it may be necessary to filter and then warm the stream after it has left the final saturator. The effluent stream may now be treated as a gas stream and metered by previously described techniques into other gas streams.

If saturation is attempted at temperatures much above room, the possibility of recondensation in connecting lines should not be overlooked. In cases such as this, maintenance of heated lines all the way from the saturator to a point where dilution removes this necessity may be required. In normal industrial hygiene work, concentrations of this order should not be needed.

Before passing to the treatment of liquid mixtures, reference should be made to the diffusion method of McKelvey and Hoelscher.[7] This apparatus, which is conveniently constructed of glass, and maintained in a constant temperature bath, contains the liquid to be vaporized in a lower container, about half-full, and its vapor is picked up in the gas stream passing through an upper chamber as it continuously diffuses up through a center connecting tube. With this diffusion cell extremely dilute gas mixtures can be produced continuously over a wide range of concentrations. Use of diffusion cells has been critically reviewed by Altshuller and Cohen[8] who prefer the Stefan-type cell which has no liquid reservoir, but stores liquid in the lower sealed end of the diffusion tube.

Liquid Mixtures

With impure liquids, and with liquid mixtures, the vaporization may be expected to approximately follow Raoult's law (actually Raoult's law is exactly followed by very few mixtures) which states that the partial pressure of a vapor above a liquid is proportional to its vapor pressure in the pure state at that temperature multiplied by its mole fraction in the liquid mixture. A distillation is thus continuously occurring and the composition of both the vapor and the liquid from which it is being generated are undergoing change. For this reason, other methods are preferable for vaporizing impure liquids and liquid mixtures such as displacement and subsequent vaporization on a continuous basis.

A simple method which has been used many places for this purpose is the use of a clock motor to lower a bob of accurate dimensions into a cylinder of liquid, displacing a uniform amount of liquid from the cylinder. The liquid is subsequently and continuously vaporized on a heated wick. The liquid thus evaporated is representative of the composition of the original liquid. Care

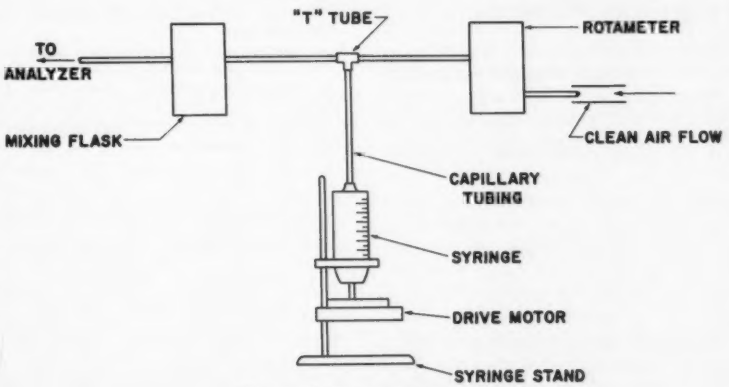

FIGURE 9. Davis Calibrator.

must be taken in the design of such an overflow system to avoid siphoning or capillary action which can result in an intermittent pulsing type of liquid flow.

Motor Driven Syringe

A more sophisticated and basically more satisfactory method of displacement is the use of a motor-screw-driven syringe. A commercial version of this device is available in the Davis Calibrator, the basic components of which are shown in Figure 9. This method is satisfactory with either a liquid or a gas fill in the syringe. The particular assembly illustrated is for use with gas since no vaporizer is shown in conjunction with the syringe feed. A constant speed motor, coupled to a gear reducer, driving an accurately cut screw to which is coupled a syringe of uniform bore will result in a constant displacement of the content of the syringe. The Davis unit uses a one rpm drive on a 40-thread-per-inch screw coupled to a 50-ml syringe of 17-ml-per-inch volume, so the displacement is 17/40 ml (0.425 ml) per minute. With gas in the syringe and an airflow of 4.25 liters per minute, a concentration of 100 ppm would result. With liquid, an additional calculation would be involved to relate liquid volume displaced to gas volume generated:

$$V_G = \frac{V_L \times d_L \times 22{,}400 \times 760 \times T}{MW_L \times P \times 273.1} \qquad (7)$$

where

V_G is volume of gas generated, ml per minute,
V_L is volume of liquid displaced, ml per minute,
d_L is density of liquid at temperature T,
MW_L is gram molecular weight of liquid,
P is atmospheric pressure, mm Hg,
T is temperature of liquid, degrees K.

If the syringe is discharging gas, it may be fed directly into the stream of metered air as indicated. If the syringe is to discharge liquid, a heated vaporizer should be located in the metered air stream to receive the output of the syringe.

A third method of uniform liquid displacement is that described by Calcote.[9] Liquid feed is accomplished by its displacement from a tube by mercury which is in turn displaced from its reservoir by a constant flow of air. The constant air flow is achieved against the increasing back pressure of the mercury column by use of a sonic orifice. The primary advantage of this system over those described previously is the ease with which the delivery rate can be varied by adjustment of the controlled pressure applied to the upstream side of the sonic orifice. A further advantage is the extended period over which such a device may be used if a long liquid tube is employed. This is especially notable when it is compared to the limited length of the average syringe.

All of these liquid displacement methods can be seen to be limited to the amount of liquid stored in the reservoir, and to this extent are batch methods. However, the time of exhaustion can be so long compared to the time necessary for refill and restart that for practical purposes the liquid displacement procedures may be continuous methods.

References

1. Gilliland, E. W.: *Encyclopedia of Instrumentation for Industrial Hygiene*, p. 52, University of Michigan, Ann Arbor, Michigan (1956).
2. Stead, F. M., and G. J. Taylor: Calibration of Field Equipment from Air Vapor Mixtures in a Five-Gallon Bottle. *J. Ind. Hyg. & Toxicol. 29:* 408 (Nov. 1947).
3. Setterlind, A. N.: Preparation of Known Concentrations of Gases and Vapors in Air. *Am. Ind. Hyg. Assoc. Quart. 14:* 113 (June 1953).
4. Baker, W. J., and T. L. Zinn: Preparation of Gas Calibration Samples. *Perkin-Elmer Instrument News 11:* 1 (summer 1960).
5. Oberfell, G. G., and R. P. Mase: An Automatic Compensating Flow Meter. *J. Ind. Eng. Chem. 11:* 294 (April 1919).
6. Mase, R. P.: U. S. Patent 1,494,856 (May 20, 1924).
7. McKelvey, J. M., and H. E. Hoelscher: Apparatus for Preparation of Very Dilute Gas Mixtures. *Anal. Chem. 29:* 123 (Jan. 1957).
8. Altshuller, A. P., and I. R. Cohen: Application of Diffusion Cells to the Production of Known Concentrations of Gaseous Hydrocarbons. *Anal. Chem. 32:* 802 (June 1960).
9. Calcote, H. F.: Accurate Control and Vaporizing System for Small Liquid Flows. *Anal. Chem. 22:* 1058 (Aug. 1950).

Personnel Protection Program for Industrial Use of Krypton-85

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Krypton-85 has recently replaced radium bromide as the residual ionization source in cold cathode gas discharge tubes manufactured by the Western Electric Company. This change was carried out to reduce radiation exposure to personnel during manufacture and use of the tubes. The personnel protection program, which had been in effect for radium bromide, was modified to conform to the special properties of krypton-85. This modified program consists of area monitoring, personnel monitoring, and occupational medical examinations. Some occupational exposure data are given and are compared to similar data for radium bromide. The use of krypton-85 has reduced the radiation exposure of the employees below the previously low levels encountered when radium bromide was used.

Introduction

KRYPTON-85 used in industry introduces a possible radiation exposure of personnel. This article discusses the present personnel protection program accompanying the use of krypton-85 by the Western Electric Company in electron tube manufacture.

Formerly radium bromide was used in cold cathode gas tubes manufactured by this company to stabilize the breakdown voltage and promote rapid establishment of the discharge. Recently, conversion to krypton-85 in place of radium bromide[1] was carried out for two primary reasons:

(1) To reduce radiation exposure during tube manufacture.

(2) To reduce external radiation from completed tubes.

A personnel protection program accompanying the use of radium in electron tube manufacture was set up when radium bromide was first introduced some years ago. Since krypton-85 is a gaseous material and is handled differently from radium bromide, a modified personnel protection program was inaugurated to conform to the special properties of krypton-85.

Radiations are negligible from Western Electric electron tubes containing krypton-85 as normally installed in use. Therefore special precautionary measures by the user are unnecessary unless required by local regulations.

Licensing

Since krypton-85 is a radioactive material which is a by-product of nuclear reactors it can only be used under a license issued by the Atomic Energy Commission. Title 10, Chapter 1, Part 30, of the Code of Federal Regulations[2] contains the provisions for issuance of a license to manufacture, produce, transfer, receive, acquire, own, possess, use, import or export by-product material. The licensing provisions assure control of the by-product material and set up an inspection and regulatory procedure to maintain safe plant operating conditions. At the present time, a specific license is not required by the general public to possess or use tubes containing less than five microcuries each of krypton-85.[2]

Properties of Krypton-85

In Table I, some properties of krypton-85[3, 4] are given along with corresponding properties of some other radioactive materials for comparison.[5, 6, 7] Table II gives the range of β rays from krypton-85 in various materials,[8] while Table III gives thicknesses of various materials which reduce the intensity of γ rays from krypton-85 to one-tenth their incident intensity.[9] The data in Tables II and III provide a basis for designing shields against the radiations from krypton-85.

Krypton-85 represents a much smaller internal radiation hazard to the human body than other available radioactive materials because it is gase-

TABLE I

Properties of Krypton-85 Compared to Some Other Materials[3, 4, 5, 6, 7]

Property	Kr-85	Co-60	Cs-137	Radium*
Atomic number	36	27	55	82–88
Atomic weight	85	60	137	206–226
Half-life	10.3 yr.	5.27 yr.	33 yr.	1620 yr.
α-emission MeV	—	—	—	4.8, 5.3, 5.5, 6.0, 7.7
β-emission MeV	.672 max.	.314 max.	.51, 1.2 max.	.65, 1.2, 1.8, 3.1 max.
γ-emission MeV	.517	1.17, 1.33	.661	.05, .18, .77, 1.8
α % of total	0.0	0.0	0.0	75
β % of total	99.54	33	51	17
γ % of total	0.46	67	49	8

* In equilibrium with its decay products.

TABLE II

Maximum Range of β Rays from Krypton-85[8]

Material	Max. Range in Inches
Lead	.007
Iron	.012
Aluminum	.025
Glass	.03
Concrete	.04
Lucite	.055
Water (or tissue)	.1
Air	52

TABLE III

Thickness of Various Materials Necessary to Reduce γ-rays From Krypton-85 to One-tenth Intensity[9]

Material	Thickness in Inches
Water (or tissue)	9.2
Carbon	6.8
Concrete	4.6
Aluminum	4.0
Iron	1.7
Lead	.52
Tungsten	.37

ous, insoluble in body fluids, and chemically inert. Therefore, any krypton-85 brought in contact with the body is not bound there, but is soon dispersed under normal conditions.

Maximum Permissible Exposure

Industrial exposure to krypton-85 can be of two types. The first type is exposure to gamma and beta radiations emanating from sealed sources such as storage tanks and completed electron tubes, and the second type is exposure from escaped krypton-85 in the air. The general legal regulations concerning these exposures are given in the Code of Federal Regulations Title 10, Chapter 1, Part 20.[10] The various states have legal regulations of their own, and these may be more restrictive than the Federal Regulations in some cases. Limits on radiation exposure from sealed sources[10] are given in Table IV. The maximum permissible concentrations for krypton-85 in air[10] are given in Table V. The term "restricted area" in this table refers to an area, access to which is controlled by radiation protection personnel, whereas the term "unrestricted area" refers to residential areas and other places access to which is not under such control. In industrial installations, manufacturing and storage areas could be considered restricted areas, while offices and the grounds could be considered unrestricted areas.

Personnel Monitoring

In order to assure that the above limits are being met, external radiation and concentration of krypton-85 in the air must be measured. For personnel monitoring, film badges and pocket ionization chambers are commonly used. A flow-through ionization chamber is a preferred method for measuring the concentration of krypton-85 in air.

For routine personnel monitoring, pocket ionization chambers are used in the present program.

TABLE IV

Federal Maximum Permissible External Exposure Rems per Calendar Quarter

1. Whole body; head and trunk; active blood forming organs; lens of eyes; gonads	1¼
2. Hands and forearms; feet and ankles	18¾
3. Skin of whole body	7½

Note: Exposure to whole body may reach 3 rems in a given calendar quarter, provided the accumulated dose does not exceed 5(N-18) rems where N stands for the individual's age in years, and also provided required records are kept.

TABLE V

Maximum Permissible Concentrations of Krypton-85 in Air

Type of Area	Maximum Permissible Concentration	Exposure Basis
Unrestricted	$3 \times 10^{-7} \mu c/cm^3$	Continuous
Restricted	$1 \times 10^{-5} \mu c/cm^3$	40 hours per week

FIGURE 1. Automatic exhaust and gas fill machine for use of krypton-85 by Western Electric Company in electron tube manufacture.

They are preferred for this program because they permit the most convenient and rapid acquisition of exposure data. The pocket ionization chambers are not as useful for monitoring β rays as film badges are, but, since it is found that β radiation from krypton-85 contained in storage tanks or completed electron tubes is negligible, this is not a serious limitation. Film badges were used in addition to pocket ionization chambers during the establishment of the krypton-85 personnel protection program, but are now used only on a spot check basis.

Personnel monitoring is part of the general occupational medical examination program. Only a small fraction of the employees of the company is exposed to krypton-85; all of these are monitored with pocket ionization chambers according to the following schedule. Employees new to the program are monitored weekly for 13 weeks. If an employee has an average dose less than 40 milliroentgens per week, he is thence forward monitored for one week every 13 weeks. If an employee has an average dose from 40 to 100 milliroentgens per week, he continues to be monitored weekly. If an employee has any one level of exposure above 100 milliroentgens per week, he is assigned to another job while the case is investigated by the Industrial Hygienist.

Area Monitoring

The minute trace amount of krypton-85 used in electron tube manufacture is an integral part of the neon-argon gas mixtures as purchased from the supplier in standard rare gas pressure cylinders. It is injected into the electron tubes by an automatic exhaust and gas fill machine directly from the cylinders through a gas metering system, Figure 1. Since gas leaks are possible when cylinders are connected, it is necessary to check for radioactive gas leaks. For this purpose a portable hand carried air monitor of the continuous sampling type is used, Figure 2.[11]

Most instruments of this type are sensitive to flames, cigarette smoke, dust, and radio frequencies. A modification of this instrument, incorporating a radio frequency filter in the 110-volt power input removes enough of the interference due to the radio frequencies and "line noise" so that a leak can be readily detected. Since the portable air monitor does not have the sensitivity required to detect the maximum permissible concentration of krypton-85 in the air for unrestricted areas (3×10^{-7} $\mu c/cm^3$), a more sensitive air monitor is necessary to assure maximum personnel protection. The continuous air sampling sensitive air monitor, Figure 3, has a built-in particle filter and an electrostatic filter which permit detection below the maximum permissible concentration with only slight interference from spurious disturbances.[12] Mounted on a tool cart, it can be relocated in various areas with a minimum of effort. It can be set up with a recorder to record the radiation level in various

FIGURE 2. Machine setter checks for gas leak at pressure cylinder connection using portable radioactive gas detector. An Atomic Accessories Tritium Monitor Model TSM-91, calibrated for krypton-85, is being used.

manufacturing areas and to monitor strategic locations inside and outside the plant periodically.

The production area, packaging and shipping area, gas storage area, and analytical laboratory are designated "restricted areas". They are surveyed at least monthly using a portable survey meter to determine if there is excessive radiation from concentrations of krypton-85 in sealed sources or from leaks. These areas are identified by approved caution signs[10] and are outlined by a tape marking on the floor. A record of the surveys is kept by the Industrial Hygienist.

Occupational Medical Examinations

Exposure to radiations from radioactive materials may produce serious burns and cancer, while the blood and blood-forming organs can be profoundly affected. Table VI gives some symptoms, conditions, and diseases associated with severe radiation exposure. Maximum permissible exposure limits have been set so that there is very slight possibility of these symptoms ever being observed. The protection program is designed to insure that the actual exposure is well below these maximum limits. Nevertheless routine occupational examinations are performed; the tests used are listed in Table VII.

The employee is then questioned about any subjective symptoms, and all subjective and objective signs are noted on the employee's chart. Records of occupational examinations are kept with the employee's medical record in the medical department until five years after his termination of service. If any suspicious findings are revealed during this examination the employee is immediately assigned to a job in an area removed

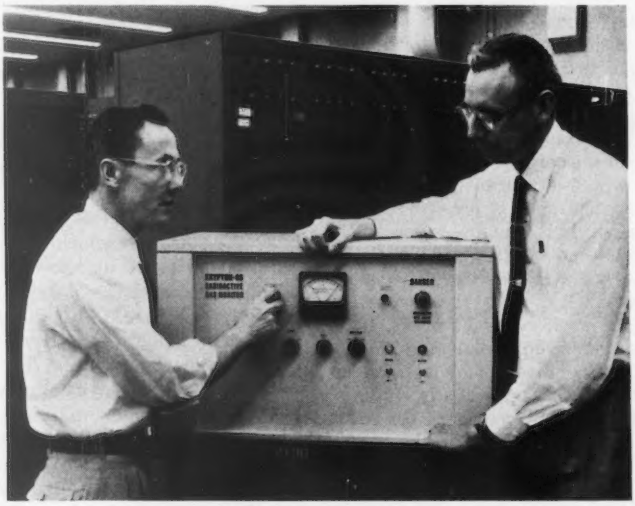

FIGURE 3. Messrs. Cassidy (on left) and Bartholomew discussing sensitive air monitor that is used to measure the concentration of krypton-85 in the plant atmosphere. The instrument is a Tracerlab Krypton-85 Monitor.

TABLE VI

Symptoms, Conditions and Diseases Associated with Severe Radiation Exposure

1. Severe dermatitis or destruction of skin and nails.
2. Radiation burns.
3. Necrosis of bones.
4. Anemia, leukemia, leucopenia.
5. Genetic changes or sterility.
6. Cancer.
7. Death.

TABLE VII

Occupational Examination Tests

1. Check pocket chamber readings.
2. Record temperature, pulse and respiration.
3. Record blood pressure.
4. Record menstrual history on all females.
5. Urinalysis and complete blood count.
6. Physical examination, including inspection of skin, nails, ears, eyes, mouth, gums, teeth, throat, and heart.
7. X-ray chest (routinely, depending on age).

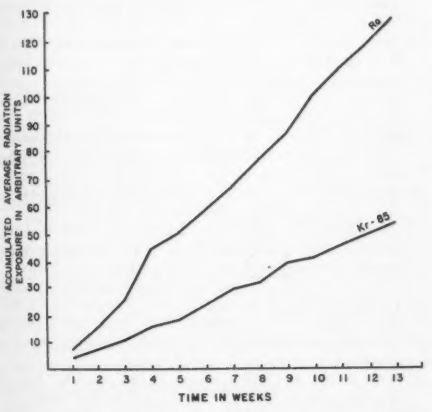

FIGURE 4. Comparison of average radiation exposure from radium and krypton-85 in electron tube manufacture.

from the area of exposure, and the employee is kept under observation.

Occupational Exposure Data

Figure 4 gives some average occupational exposures at the Allentown Works to krypton-85 radiations for a typical 13-week period compared to similar data from past records when radium bromide was in use. The data presented here are for workers who are assigned to the handling and use of krypton-85. Workers not so assigned are found to have exposures not higher than background. It is seen that typical average external exposure to krypton-85 is about 40 per cent that of radium.

Marking, Shipping, and Disposal of Krypton-85 Tubes

Electron tubes must be marked according to the provisions of the specific license under which they are manufactured. Individual tube containers must be marked according to CFR Part 20, paragraph 20.203f.[10] For krypton-85 this requires individual tube carton marking on all tubes which contain more than 0.1 microcurie of krypton-85.

Shipping containers for common carrier transport are marked according to Interstate Commerce Commission regulations.[13] The ICC diamond-shaped label is required on the outside surfaces of packages of gamma-emitting materials when the gamma radiation at the outside surface of the package exceeds 10 milliroentgens per 24 hours. When the label is required, the radiation level in milliroentgens per hour at a distance of one meter must be recorded on the label. Parcel post shipments containing not more than 1.3 millicuries may be made provided the package is properly marked.[13]

Disposal of by-product radioactive material must be in accordance with CFR Title 10, Part 20, paragraph 20.301 to 20.305. Disposal in sanitary sewerage systems and by burial in the soil

TABLE VIII

Summary of Protection Program

Item	Schedule	Remarks	Responsible for Records
Personnel Monitoring	Weekly or quarterly	Pocket chamber used	Medical Dept.
Area Monitoring			
a. Work areas	Daily and when tanks are changed	Hand carried air monitor plus sensitive air monitor	Industrial Hygienist
b. Exhaust stack	Semiannually	Sensitive air monitor	Industrial Hygienist
Storage areas	Monthly	Portable survey meter	Industrial Hygienist
Occupational Exam.	Quarterly	—	Medical Dept.

is permitted under certain restrictions. Disposal by incineration is prohibited. Application for permission to use special disposal methods may be made to the AEC.

The present Western Electric Company tube disposal program, authorized by the AEC, is as follows: In the manufacturing plant, tubes are crushed under a hood which is vented to the outside atmosphere. The crushed material is examined for residual radioactivity, and, if none is found, is disposed of as normal scrap. Any residues found radioactive are encased in concrete and disposed of at sea. Tubes in the field may be broken in a well ventilated place and then disposed of as normal broken electron tubes at rates not exceeding 100 tubes per week from any one location.

Public Relations

Only the public relations organization is authorized to give information to the public and the press regarding the use of radioactive materials in the plant and the personnel protection program used. In case of any accident or overexposure, it is authorized to discuss the incident with the press and public. It is the policy in dealing with the public in these matters to be completely frank and above-board, and to withhold no information which bears on the health and safety of the employees and the public.

Conclusions

The use of krypton-85 in the Western Electric Allentown Works has reduced the exposure of the employees below the previous low values encountered when radium was used. The personnel protection program described is summarized in Table VIII, and is designed to maintain a complete history of personnel exposure to radiation and to keep this exposure to the lowest possible level.

References

1. Cassidy, G.: Radioactive Krypton in Cold Cathode Tubes, *The Western Electric Engineer 4:* 29 (Jan. 1960).
2. *Federal Register, Code of Federal Regulations.* Title 10, Chapter 1, Part 30, "Licensing of By-product Material" (Jan. 10, 1956).
3. Strominger, D., J. M. Hollander, and G. T. Seaborg: Table of Isotopes. *Rev. Mod. Physics 30:* 585 (1958).
4. Geiger, K. W., J. S. Merritt, and J. G. V. Taylor: New Branching Ratio for Kr-85. *Nucleonics 19:* 97 (Jan. 1961).
5. Data on Co-60, Cs-137 and Radium were compiled from several sources, primarily references 6 and 7.
6. National Bureau of Standards Handbook 54 *Protection Against Radiations from Radium, Cobalt-60 and Cesium-137.* U. S. Government Printing Office, Washington, D. C. (Sept. 1954).
7. Forsythe, W. E., Ed.: *Smithsonian Physical Tables.* 9th Ed. (1954).
8. *U. S. Public Health Service: Radiological Health Handbook.* Rev. Ed. (1957) PB 121784, Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C.
9. *Los Alamos Handbook of Radiation Monitoring.* LA-1835 3rd Ed., U. S. Government Printing Office, Washington, D. C. (1959).
10. *Federal Register, Code of Federal Regulations.* Title 10, Chapter 1, Part 20, "Standards for Protection Against Radiation", January 16, 1957; also amendment to Title 10, Chapter 1, Part 20, "Standards for Protection Against Radiation", September 7, 1960.
11. Eutsler, B. C., et al.: Instruments for Monitoring Tritium in the Atmosphere. *Nucleonics 14:* 114 (Sept. 1956).
12. Brinkerhoff, J., et al.: Continuous Air Monitor for H-3. *Nucleonics 17:* 76 (Feb. 1959).
13. *Handbook of Federal Regulations Applying to Transportation of Radioactive Materials.* U. S. Government Printing Office, Washington, D. C. (May 1958).
14. National Bureau of Standards Handbook 69: *Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air and Water for Occupational Exposure.* U. S. Government Printing Office, Washington, D. C. (June 1959).
15. Wilson, E. J.: Manipulation of Radioactive Gases in High Vacuum Apparatus. *Vacuum 4:* 303 (Feb. 1957).
16. Walton, G. N., Ed.: *Glove Boxes and Shielded Cells.* p. 143, Academic Press, New York (1958).

Fifth Annual Institute for Physicians in Industry

THE COLUMBIA UNIVERSITY SCHOOL of Public Health and Administrative Medicine has announced its Fifth Annual Institute for Physicians in Industry to be held March 12 through March 17, 1962. This Institute will follow quite closely the pattern and material of the preceding Institutes. Subject material will cover epidemiology, toxicology, ionizing radiation, air pollution, and a general review of occupational medicine based on the subject matter of the specialty board examinations. In order that those attending the Institute may derive maximum benefit from the presentations, enrollment will be limited as in the past.

Inquiries and requests for enrollment forms should be addressed to:

The Program of Continuation Education-Occupational Medicine
Columbia University School of Public Health and Administrative Medicine
600 West 168th Street, New York 32, New York.

Design of a Radon Exposure System

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A laboratory facility for the exposure of animals (mice) to known concentrations of radon in an inhalation toxicity chamber is described in some detail. A dynamic system is used providing for intermittent or long-term exposures. De-emanation of a radium chloride solution by aeration is used as the source. Exposures to radon provides diffuse irradiation of the respiratory tract by an alpha-emitter as contrasted to discrete particulate sources.

Introduction

THE study of the effects of inhaled radon gas is of interest from both an academic and a practical standpoint. In the former instance radon is unique in being an alpha-emitting gas, and is therefore a diffuse irradiator in the respiratory tract, whereas other alpha-emitters which have been studied in inhalation exposures have been in the form of particulate or discrete irradiators. Comparisons between diffuse and discrete dosage in the respiratory tract can add further light to the important question of the significance of localization of alpha-emitters and subsequent intensified irradiation of limited areas.

The practical problem arises in connection with the uranium mining industry. As a member of the uranium decay series, radon is found in all uranium mines. Its control is not difficult; adequate ventilation of the working faces, tunnels and shafts will serve to dilute or sweep out any radon released during drilling, shooting, or mucking operations. In the larger mines, however, the amount of ventilating air required may be very large and adequate ventilation may be difficult to achieve, particularly if radon is diffusing from other surfaces in addition to those being worked.

It is important, therefore, to establish the reliability of the currently used limit for radon levels, and to determine the safety factor associated with this limit, since in some mines concentrations are occasionally found which greatly exceed permissible levels.

Background

Since the inception of studies on inhaled radioactive materials at this laboratory, there has been marked interest in radon as a test substance. Morken has studied both the acute toxicity[1] and chronic toxicity in mice,[2] to establish baseline information for the comparison of diffuse-irradiator and localized-irradiator concepts under acute exposure conditions. These studies also served to indicate what levels of radon might be tolerated for relatively long periods by mice (up to the normal lifespan of the mouse). One of the important criteria for injury in long-term studies is the possible enhancement of lung tumor incidence, since a great deal of discussion has centered around the fate of the Joachimsthal miners, many of whom are said to have died from radiation-induced lung cancers. It was evidently necessary, then, to develop a radon exposure system which would reliably provide known and reasonably uniform air concentrations of this gas for long periods of time.

Design Criteria

In developing a system for long-term exposures of large numbers of mice to radon atmospheres, advantage was taken, as far as possible, of Morken's experiences with his small-scale acute exposure system, but it was soon evident that marked differences existed between the two systems. First, large animal populations are necessary for statistical significance of any results bearing on lifespan shortening or tumor incidence. Second, it is desirable to expose the animals for as many of the 168 hours in a week as possible. Third, for several reasons (among them gamma activity buildup and concentration control) the recirculation system used by Morken was deemed unfeasible, for a scaled-up version.

The final arrangement is shown schematically in Figure 1. The major components of the exposure system are the chamber and its controls, the radon generator, and the sampling system. All components were installed in the Cold Animal Room of the Radioactive Inhalation Laboratory.[3] This highly specialized laboratory pro-

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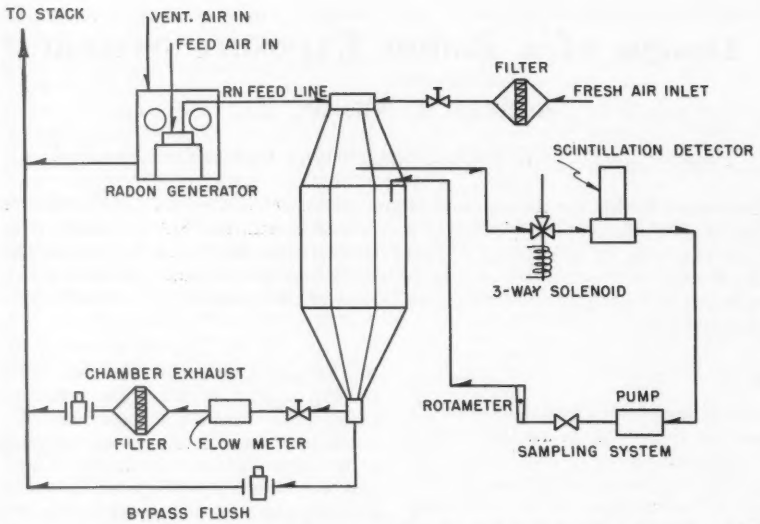

FIGURE 1. Schematic diagram of the radon inhalation exposure system, showing the flow of ventilating air and radon into the chamber, the chamber concentration sampling system, and the chamber flow controls.

vides a number of the facilities needed for the safe use and handling of considerable quantities of radium and radon.

The Radon Exposure Chamber

The chamber is the hexagonal style which has been described elsewhere.[4] Two additional shelves were added to the basic design in order to contain the desired number of animals, and extra care was taken to ensure that there was no leakage in the chamber structure. These measures included taping all rigid joints in the chamber walls with Scotch brand #471 plastic film tape, sealing all shelf support rod penetrations with Kalk-Kord (Sears, Roebuck), and meticulously cementing a closed-cell neoprene gasket to the door. Such careful precautions were necessary in order to eliminate as much as possible of the undesirable leakage air so that total airflow through the chamber could be minimal. This in turn would permit a minimal amount of radium in the generator system.

This unit has a maximum capacity of 240 mice, and although usual practice is to condition the incoming air in animal exposure chambers, in this case it was unnecessary because (1) the animal heat load was low, and (2) the room in which the chamber was erected was already adequately conditioned for mice, and heat transfer through the chamber walls was sufficient to yield temperature equilibration between inside the chamber and out. A cooling coil in the inlet line permits addition of air cooling should it prove necessary in the future.

The flow rate through the chamber is very low, fifty liters per minute, for a turnover rate of 2½ air changes per hour. The rate is controlled by a plug cock for rough adjustment and a gate valve for fine. It is measured by a 2″ venturi flowmeter which has a 1″ throat diameter. A negative pressure of about 0.02″ H_2O is maintained at all times to ensure that any leakage will be inwards. This is established by throttling the incoming air with a gate valve.

The chamber exhaust is connected to the Hot Blower System of the Radioactive Inhalation Laboratory through a glass-fiber filter, the purpose of which is to protect the high-efficiency filters on the blower system. A by-pass flushing line is provided for rapid flushing of the chamber in the event it were necessary to open it quickly. The by-pass eliminates any need for altering the valve settings on the normal flow path, which are not easy to reset to exactly the same values.

The Generator System

The generator system is similar in many regards to dispersal systems used in studying toxicity of solvents or other materials having appreciable vapor pressures. Because of the severe health hazard of radium, however, a number of

complications entered into the design of this system.

The size of the system was established by the requirements of the experiment. Previous experiments had shown that the optimal concentration of radon in the chamber would be between 10^{-7} and 10^{-6} curies/liter, and 5×10^{-7} was selected as a target concentration. In order to hold the amount of radium to a minimum, it was evidently desirable to have as little air as possible passing through the chamber, and it was determined that this amount should not be less than 50 liters/minute for the good of the animals. A simple calculation yields a radon evolution rate of 25 μc/min.

Previous experience indicated that to remove the radon from radium by simple bubbling, without any supplemental heat, at least 200 mg of radium would be needed. To minimize the formation and precipitation of radium sulfate, the radium chloride was ordered with a barium-to-radium atom ratio of 1000:1. These salts were to be dissolved in 0.5*N* HCl, in a further effort to prevent deposition of the radium and consequent increased difficulty in removing radon. This set the minimum solution volume at about 1000 ml.

For several reasons, it was preferable to have two equal-sized generators rather than one large one. Among these reasons were the ease of obtaining standard glassware for holding the solution, the greater ease of handling pieces of smaller shields (although the total amount of lead required was greater), and the reduction in the radiation problem if a solution vessel broke.

The design used is shown in Figure 2. The shield is composed of cast rings of lead, with a thickness of four inches. Of course, as long as deemanation (*i.e.* removal of radon) occurs there is no need for shielding, but this is not a reasonable risk to take, since equilibrium is reached quite quickly, and in only a few days the gamma level from this amount of radium becomes a problem. The holes through the shield permit direct observation of solution level and generator performance. Radiation through the holes is minimal, and furthermore mirrors are used to make such observations, so that personnel exposure is negligible.

The principle of "defense in depth" against accidents is exemplified in the solution vessels. It is well known that glass is dangerously degraded by radiation, becoming extremely brittle. Pyrex brand glass is considerably better in this regard than ordinary lime glass, but is still embrittled to a certain extent. To guard against the contingency of breakage, the solution is held

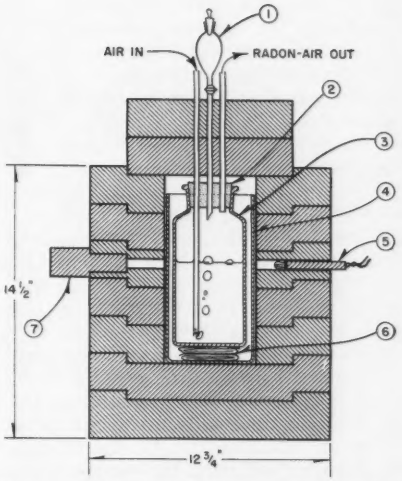

FIGURE 2. Radon generator and shield. 1. Solution make-up (Corning No. 6340). 2. Rubber stopper. 3. Radium solution vessel (Corning No. 1280). 4. Solution retention jar (Corning No. 6920). 5. Level-viewing light. 6. Surgical sponges. 7. Level-viewing port. The shield itself is made up of nested lead rings which provide at least 4 inches of shielding all around.

in a carefully stress-relieved Pyrex jar, which in turn is placed in another heavy Pyrex jar. The shield itself constitutes a third line of defense should both jars fail.

To guard against inadvertent escape of either radium or radon into the laboratory, the generators are housed in a gloved box which is ventilated by the Hot Blower System previously mentioned. A negative pressure of at least ½" H_2O is maintained, and although the box is relatively small, a flow rate of 10–15 cfm is maintained so that any escaping radon will be swept out before decay and subsequent deposition of the daughters can occur in significant amounts; otherwise, unnecessarily high gamma levels would develop in the box after a leak.

A schematic diagram of the entire generator system is shown in Figure 3. Building compressed air is brought in at 50 psi, and regulated down to 3 psi. A safety valve, set at 4 psi, is situated just downstream from the regulator to prevent overpressure on the generators if the regulator should fail. A normally open solenoid valve serves as the primary shutoff. The philosophy here is that the "safe" condition is continuous de-emanation of the radium. As discussed in Ref. 4, essentially total disaster is necessary to cause a stoppage of ventilation in

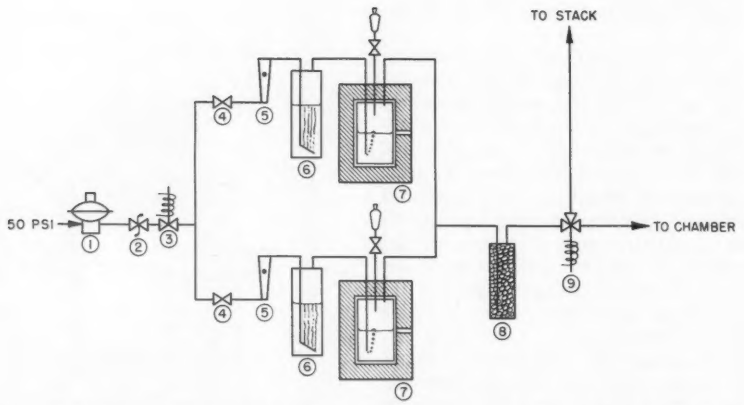

FIGURE 3. Schematic diagram of the radon generator system. 1. Pressure regulator, 0–10 psi, Hoke #804. 2. Safety valve, 4 psi; James-Pond-Clark #500. 3. Solenoid valve, normally open, Skinner #V5D 4850. 4. Needle point control valve, Hoke #D309. 5. Rotameter, Fisher and Porter, Size 2, Fig. 130, C-clamp. 6. Conditioner bubbler, Will Corporation #15381 gas washing bottle. 7. Radon generator and shield. 8. Soda lime acid absorber. 9. Selector solenoid valve, Skinner #V5D4350.

this Laboratory. Therefore, if the solenoid should fail for any reason, flow would continue through the generators and the radon evolved would be carried up the stack; gamma level buildup in the solutions would not occur.

The rate of flow through the generators is very low, 150 cc/min serving to de-emanate almost quantitatively. This is due largely to the limited solubility of radon, so that it is easily swept out of the radium solution. Flow is controlled by Hoke needle-point valves and measured by rotameters. This flow rate was selected as the minimum amount of air that would give satisfactory de-emanation without appreciable spatter and aerosolization (but see Performance section).

Before passing to the generators, the air is preconditioned in gas washing bottles which have fritted glass bubblers. These conditioners are filled with 0.5*N* HCl, and serve to humidify and acidify the air going to the radium solutions. By this treatment loss of water and acid from the radium solutions is minimized.

The conditioned air is discharged well below the surface of the generator solutions in order to cause enough stirring to bring radon-rich solution to the surface for release of the gas. Provision is made at the generators for adding makeup liquid, which is required from time to time in spite of the preconditioning of the air.

Air from both generators then passes through a soda lime acid absorber to remove any acid fumes carried over with the radon. This was found necessary to protect the metal parts of the selector solenoid valve which directs the radon-laden air stream either to the chamber or to the stack. The "fail-safe" position on this valve sends the radon up the stack so that there is no possibility of inadvertent filling of the chamber with radon in the event of valve failure.

The Sampling System

Routine monitoring for air concentrations of radon is hampered by the presence of the daughters, which have a tendency to plate out on or in the sampler thus causing elevation of the alpha background. The system used in determining chamber concentrations compensates in part for this problem, but for careful evaluation of the radon level it is necessary to fall back on more classical methods; chamber air is drawn through a filter into an evacuated ionization chamber, and the amount of activity thus collected is determined with a vibrating reed electrometer.

The routine assay, however, serves quite well to evaluate the stability of concentrations in the chamber over the course of the long operating periods. Air is drawn from the chamber, through a filter and into a scintillation alpha detector. This detector is virtually the same as the alpha monitors described by Morken and Wilson,[5] except that the detector looks at a volume of radioactive gas rather than a filter paper. Its construction is shown in Figure 4.

The motive power for the sampling system

is a White Mist #50 aquarium aerator pump, with its inlet modified to permit in-line installation. It was selected because of its quietness and high reliability. Air is sampled at a rate of one liter per minute, although the actual magnitude of the rate is not critical. This gives a filling time of the detection volume of the scintillator of about twenty seconds. The sampled air is ultimately discharged back into the chamber at about the same place as it was sampled.

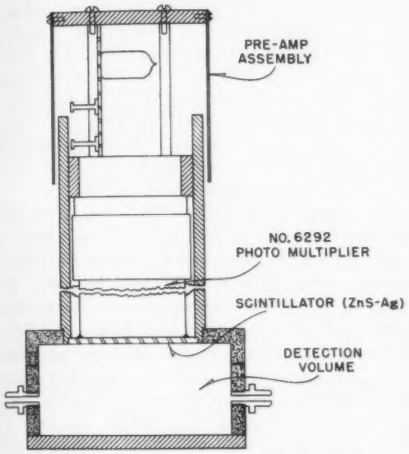

FIGURE 4. Radon concentration detector.

In order to minimize the confusion attendant upon the buildup of daughters in the detection volume the sample is drawn on an intermittent clock-controlled basis. The cycle commences with a background determination which lasts three minutes, with the sampling line open to room air. Then a three-way solenoid valve opens to the chamber sampling line, and a sample is drawn for fifteen minutes. At the end of the sampling period the three-way valve closes the chamber sampling line and reopens to the atmosphere, so that room air is drawn in (at the same rate) to flush the detection volume. This cycle is repeated hourly, 24 hours a day. The counting signals from the detector are fed to an Esterline-Angus recorder which records the background, rate of rise of activity in the detection volume, peak activity reached, and rate of initial flushing (for two minutes after the solenoid switches to room air). A typical chart section is reproduced in Figure 5. It should be noted that for a forty-minute period between sampling cycles chart advancement is halted, and the pen falls along the same time line.

An attempt to control daughter deposition by

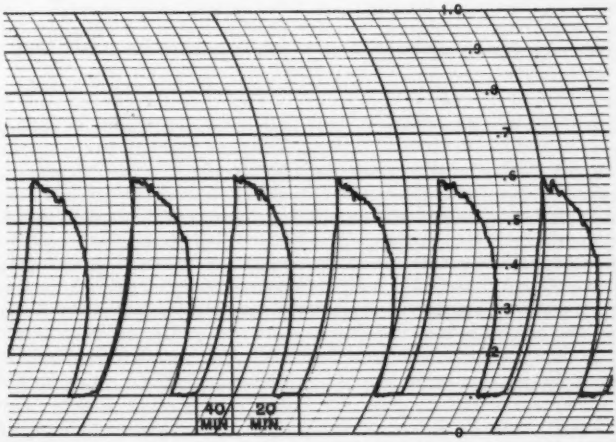

FIGURE 5. Segment of Esterline-Angus chart showing rate of build-up of activity in the sampler detection volume. Each peak represents the maximum level attained on hourly sampling; the chart is read from right to left. Note in particular the 20-minute sampling period followed by a 40-minute flushing period during which the chart is stopped. During a sampling cycle the chart is started, recording sampler background for four minutes, and then the radon-laden chamber air is admitted to the detection volume for 15 minutes. The sampler is then shifted to the flushing cycle (indicated by the abrupt change at the chart peak) and flushing continues until the next cycle. Chart advance is stopped shortly after the start of flushing.

applying a voltage across the detection volume was largely unsuccessful. The intent was that the impressed voltage would drive the presumably charged daughters to the brass base plate of the detector, so that alpha particles from subsequent decay would be unable to reach the zinc sulfide screen. Although no major investigation of the failure of this approach was made, it seems likely that the fields developed were insufficient to have the desired effect on the heavy daughter nuclei or to overcome the energy of the recoiling nuclei following decay. With additional attention to design considerations and physical principles, it seems likely that this method of controlling daughter buildup could be made workable, and would make possible continuous recording of radon concentrations which were not obscured by high daughter levels.

Operating Procedure

The routine operation of the system is relatively simple. In the chamber, the animals are housed in Den-ko Argonne-type mouse cages, (Den-ko Manufacturing Company, 2300 W. 76th Street, Chicago 20, Illinois), 10 to a cage. Sufficient food and water can be supplied to last for as long as three days. Consequently, a schedule was established which specified normal animal care (cleaning, feeding, watering) on Mondays, Wednesdays, and Fridays. Experience showed that at least four hours of flushing with radon-free air was necessary for adequate removal of the contaminated chamber air, so a seven-day program clock was set to change the selector valve to send the radon from the generators directly to the stack at four o'clock on these mornings; thus, by the time the caretaker commenced work there was no hazard associated with opening the door.

Special maintenance consists of replenishing the solution in the conditioning bubblers as needed, and in the generators, since some evaporation does occur. The former is required every four to six weeks, while the latter occurs only once or twice a year. From time to time ionization chamber samples are drawn to ascertain the reliability of the hourly records. Service on the sampling system has been very slight. The detector has needed no service whatever, and the Berkley count rate meter which operates with it has only occasionally needed a new tube. The pump has been replaced once in approximately four years; the total radiation over this period had caused hardening and cracking of the rubber valves, seats, and diaphragm.

Performance Observations

After several years of experience with this system, there are some aspects of its performance that are useful to point out. The most important of these concerns the generators themselves. Within the first few months of operation, it was noted that liquid had appeared in the soda-lime acid trap, and a concomitant elevation in gamma background. Renewing the soda-lime gave only temporary amelioration, and before the cause of this difficulty was determined, some forty to fifty milligrams of radium were "lost" from the generators. Collection of this radium by the soda-lime trap was quite efficient, and it is estimated that very little of it got as far as the chamber or into the exhaust system.

The cause of this loss turned out to be a simple problem readily solved. As first assembled, conditioned air was discharged into the generators through fritted glass bubblers very similar to those in the conditioners, the intent being to provide a maximum area for diffusion of radon into the bubbles of new air. These bubbles, however, were of very small diameter, and when they burst released a very fine spray. The remedy consisted of simply cutting the fritted disc from the end of each bubbler tube, so that a few large bubbles were released instead of many small ones. Since this modification was made, there has been virtually no carry-over of radium. Surprisingly enough, de-emanation has been just as complete with the large bubbles as with the tiny ones.

Following the loss of some of the radium, 50 mg more were added to each of the generators. The total radium in the system is estimated to be 250 mg; for operational purposes it has not been necessary to define the amount any more precisely. Only a minimum amount of barium was added in this recharging; a 1000-fold atom ratio, as in the earlier sources, would have necessitated too great a solution volume.

Another finding of some significance is that over the course of the years of operation, the available radon has decreased by a factor of two. This is attributed to crystallization of the barium, carrying with it some of the radium, rather than further loss of radium, since no additional radium has been found outside the shield. It is believed that this phenomenon has resulted from a buildup in the acidity of the generator solutions as a result of preferential evaporation of the water. The likelihood of this explanation is strengthened by the operating experience during the latter stages of a recent experiment. During its course, it was found to be increasingly diffi-

cult to maintain adequate flow through the generators, and on occasion they plugged entirely. Although no direct examination was made, unplugging efforts indicated the buildup of solids at the end of each bubbler tube. The experiment was terminated when it was no longer possible to maintain assured flow for 24-hour periods. The possibility of formation of insoluble sulfates could not be ruled out, so enough barium chloride was added to the acid solution in the conditioning bubblers to yield saturation.

For the first few days, operation seemed satisfactory, but in the course of a week enough water had been evaporated to raise the normality, reducing the solubility of the barium chloride to the extent that only a few hours of operation was possible because of plugging of the fritted discs in the conditioner bubblers. This plugging was easily remedied by flushing the fritted discs with distilled water, demonstrating that plugging was not a function of sulfate precipitation. Following this, distilled water was added to the generators in amounts sufficient to raise the solution levels nearly to the tops of the viewing ports (see Figure 2), and 0.5*N* HCl only was placed in the conditioners. Further evidence that saturation of the generator solutions was the cause of all the difficulties is shown in the record of operations for the six months following this change. There has been no plugging, and there has been a gradual increase in radon levels in the chamber.

In light of this operational difficulty, it would seem advisable to incorporate some procedure for assaying acidity in future radon generators of this type. Unfortunately, it is not feasible to do so in the existing arrangement. It is believed that the presence of barium is desirable, although results show that something less than 1000:1 atom ratio is suitable. Except for the saturation problem, this equipment has proved quite effective for inhalation studies with radon, with no problems of temperature control, respiratory infection, or other artifact obscuring the biological results. A long series of experiments is planned for the study of radiation injury from radon, with every assurance that mechanical problems will be minimal.

References

1. Morken, D. A.: Acute Toxicity of Radon. *AMA Arch. of Ind. Health 12: 435 (1955)*.
2. Morken, D. A.: The Effect of Inhaled Radon on the Survival, Body Weight, and the Hemogram of the Mouse Following Single Exposure. *University of Rochester Report, UR-593* (1961).
3. Wilson, R. H., W. F. Neuman, A. Rothstein, and J. K. Scott: Physical Plant for a Radioactive Inhalation Laboratory. *University of Rochester Report, UR-302* (1955).
4. Wilson, R. H., and S. Laskin: Improved Design for an Animal Inhalation Exposure Unit. *University of Rochester Quarterly Technical Report, UR-116*, pp. 80-86 (1950).
5. Morken, D. A., and R. H. Wilson: A Four-Channel Continuously Recording Monitor for Air-borne Alpha-activity. *University of Rochester Report, UR-576* (1960).

Errata

DESPITE THE SEVERAL STAGES OF PROOF-READING in the publication of a journal, occasional errors and omissions do slip through. On page 245 of the August 1961 issue of this Journal two such errors virtually trod on one another. In the article "Correlation of Industrial Noise Exposures with Audiometric Findings" by E. J. Schneider, J. E. Peterson, H. R. Hoyle, E. H. Ode, and Dr. B. B. Holder the acknowledgment of affiliation should have shown Mr. Ode and Dr. Holder as members of the Medical Department, The Dow Chemical Company.

In the abstract of this same article a negative was omitted from the next-to-last sentence which should have read: There was evidence that men working in jobs profiled "A" and "B" showed no more hearing loss than was expected for normal ageing.

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